Sorption and coprecipitation of copper to ferrihydrite and humic acid organomineral complexes
and controls on copper availability

Neila N. Seda^a, Faye Koenigsmark^a, Timothy M. Vadas^{a,b,*}

^aDepartment of Civil and Environmental Engineering, University of Connecticut, Storrs, CT
06269, USA

^bCenter for Environmental Science and Engineering, University of Connecticut, Storrs, CT
06269, USA

Neila N. Seda: neila.seda@uconn.edu

Faye Koenigsmark: faye.koenigsmark@uconn.edu

Timothy Vadas: vadas@engr.uconn.edu, tel: 1-860-486-5552, fax: 1-860-486-2298

261 Glenbrook Rd. Unit 3037 Storrs, CT 06269-3037 USA

* Corresponding author

Abstract

Coprecipitation of Fe oxide and organic matter in redox dynamic sediments controls the net retention and form of Cu in the solid precipitates. In this study, coprecipitation and sorption of Cu with organomineral precipitation solids formed at different Fe:organic carbon (OC) ratios were compared for net Cu removal and extractability. As more humic acid was present during precipitation of Fe, TEM images indicated smaller Fe oxide particles formed within an organic matrix as expected. In coprecipitation reactions, as the ratio of Fe:OC decreased, more Cu was removed from solution at pH 5.5 and below. However, in sorption reactions, there was an inhibition of Cu removal at low OC concentrations. As the pH increased from 5.5 to 7 and as solution phase OC concentration increased, more Cu remained dissolved in both coprecipitation and sorption reactions. The addition of Ca^{2+} , glycine, histidine and citric acid or lowering the pH resulted in more extractable Cu from the coprecipitation compared with the sorption reactions. The variations in Cu extraction were likely due to a combination of a more amorphous structure in CPT products, and the relative abundance of available Fe oxide or OC binding sites. This has implications for the assumption of additivity in binding phases and for researchers conducting binding or exposure experiments.

Keywords: sorption; coprecipitation; ferrihydrite; humic acids; organic carbon; copper

1.0 Introduction

The partitioning of Cu in sediments is controlled by many competing phases including solid and dissolved organic matter, oxides, clays, inorganic ligands, or precipitate formations such as copper sulfides or copper hydroxides (Oorts 2013). Cu fate in particular is important due to its low aqueous concentrations for acute and chronic aquatic life criterion (EPA, 2007), illustrating its toxicity at low concentrations in aquatic ecosystems. Prior to reaching receiving water bodies, Cu interacts with soils and sediments and is primarily retained through binding to organic matter at near neutral pH. In common transition landscapes between soil and aqueous systems, namely riparian zones and wetlands, stable phases of Cu in the oxic surface water and top sediment layers are sorbed to organic matter and/or Fe oxides (Sposito, 1989). In addition, various accounts of Cu release from wetlands have been correlated to a combination of colloidal Fe oxides and/or organic carbon (OC) release (Olivie-Lauquet et al., 2001; Grybos et al., 2007; Neubauer et al., 2013) suggesting the role of both solid phases in controlling Cu release. Our understanding of the chemical interactions and availability of Cu from these mixed Fe oxide, OC, and Cu phases has come from studying the reactions between two independently formed phases, e.g. sorption of Cu onto Fe oxides in the presence of OC, and not the material as it is formed *in-situ*, i.e. coprecipitation of Fe oxide, OC and Cu at one time. In environments where redox cycling stimulates turnover and coprecipitation of Fe and OC in the oxic zone (Henneberry et al., 2012), understanding the potential differences in the *in-situ* formed solids is important for predicting the fate of embedded metals such as Cu.

The formation of ferrihydrite in the presence of OC generally slows the rate of precipitation and reduces the size of the iron oxide particles (Perret et al., 2000; Pédrot et al., 2011; Henneberry et al., 2012). The presence of carboxyl and hydroxyl functional groups have

55 been shown to lead to the formation of smaller and less crystalline Fe nanoparticles within an OC
56 matrix (Gu et al., 1996; Eusterhues et al., 2008). The presence of coprecipitated OC also
57 strongly inhibits the reductive crystallization of ferrihydrite to more stable crystal forms such as
58 goethite regardless of pH, Fe:OC ratio or type of reductant added (Henneberry et al., 2012).
59 How the changes in ferrihydrite reactivity due to the formation of smaller Fe oxide particles and
60 therefore higher surface area, different crystalline structures, or the presence of OC coatings
61 (Schwertmann et al., 2005; Eusterhues et al., 2008; Henneberry et al., 2012; Reidel et al., 2013;
62 Angelico et al., 2014) alters the binding or retention of other metals such as Cu is currently
63 unknown.

64 The coprecipitation of ferrihydrite with OC likely leads to variation in the Fe oxide
65 mineral surface area and changes in Fe oxide and OC available reaction sites. Cu has the
66 potential to form a variety of bound metal species, including isomorphic substitutions, inner or
67 outer sphere oxide surface complexes, and type A (oxide-Cu-ligand) or type B (oxide-ligand-Cu)
68 ternary complexes (Hesterberg et al., 2011). In some cases, Cu sorption may be limited by
69 competition with other inorganic cations or organic matter blocking access to binding sites. In
70 studies on multicomponent systems containing ferrihydrite, leaf compost and monmorillonite, Cu
71 binding on ferrihydrite was the least abundant and was attributed to Fe oxide site blockage by
72 DOC and a lower binding affinity (Martinez-Villegas and Martinez, 2008). As well as blocking
73 oxide binding sites, Cu sorption may be enhanced in the presence of bound OC resulting in
74 additional or higher affinity binding sites (Christl and Kretzschmar, 2001; Scheinost et al., 2001;
75 Henneberry et al., 2012). While Cu coordination with OC typically has higher binding constants
76 by at least three orders of magnitude relative to Fe oxide surfaces (Martinez-Villegas and
77 Martinez, 2008), it is unclear how the presence of Cu during Fe-OC coprecipitation alters the

total Cu binding and availability which could be altered due to differences in component concentrations, reaction kinetics (Lippold et al., 2007), or physical morphology.

Most studies of copper sorption and availability have used pre-formed Fe oxides with or without the addition of OC. A few have examined coprecipitation products of Cu and Fe (Karthikeyan et al., 1997; Karthikeyan and Elliott, 1999), but none have examined how the coupled interactions between Fe, OC and Cu during precipitation could affect metal retention or release. Our goal was to assess the difference between Cu sorption and retention depending on the formation conditions, either sorption (SOR) where Cu is added to pre-formed solids or coprecipitation (CPT) where Cu is present during precipitation. In this study, we generated solids from Fe alone or with humic acids at different ratios of Fe:OC observed in wetland sediments and examined net Cu sorption to either SOR or CPT solids. Differences in Cu availability were assessed through a series of extractions depending on pH, exchange cations, or ligands. The implications for Cu retention, transport and bioavailability are discussed.

2.0 Materials and methods

2.1 Reagent preparation

Stock solutions of NaNO_3 , $\text{Cu}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, and $\text{Ca}(\text{NO}_3)_2$ were prepared from ACS grade reagents. To prevent precipitation of Fe oxides, Fe stocks were maintained at pH 2. Background Fe and Cu concentrations in all stocks were below detection. Humic acid sodium salt (Sigma-Aldrich, St. Louis, MO, USA) stock was dissolved, filtered, stored at 4°C in the dark, and dissolved organic carbon concentration measured with a total organic carbon (TOC) analyzer prior to use. Sigma Aldrich humic acid was used instead of a standard reference organic material due to the need for several grams of humic acid required for this study. In addition, it was available in a relatively pure form to demonstrate the concept of Fe:OC

precipitation products without the need for labor intensive extraction procedures from natural soils. All solutions were made using 18 M Ω deionized water (DI) and containers were acid washed in 10% HNO₃ for 24 hours and triple-rinsed with DI water prior to use.

2.2 Coprecipitation and sorption reactions

Triplicate solutions of CPT and SOR reactions were prepared in acid washed polyethylene bottles with five Fe:OC molar ratios varying from 1:0 to 1:10 and varying pH from 4 to 7. CPT solutions were prepared in the following order with 10 mM NaNO₃, Cu concentration fixed at 1 mg/L, HA added at 0, 3, 18, 36 or 60 mg/L carbon, and Fe added last at a fixed concentration of 28 mg/L in a total volume of 50 mL. These Fe and C concentrations represent typical values observed in pore waters of a local wetland. SOR solutions were prepared following the same procedure, excluding the initial addition of Cu. The pH was adjusted to the experimental pH to initiate ferrihydrite precipitation by drop-wise addition of NaOH. Samples were then placed on a rotator at 30 rpm covered to keep out light, and pH was checked after 30 minutes. Adjustment to pH was made if necessary (if any, it was less than 0.2 pH units), and samples continued to rotate for 24 h with pH confirmed at the end. For SOR reactions, 1 mg/L Cu was added and the solutions were placed on the rotator for an additional 24 h. Following rotation, all samples were centrifuged at 2450 g for 30 min prior to filtration through a pre-rinsed 0.22 μ m cellulose membrane filter. The solid precipitates were dried in an oven at 75° C for 24 h and the dry mass was recorded. Filtrates were analyzed for Cu, Fe, and DOC concentrations as detailed below. Control precipitation products with Cu and DOC only had 90-100% recovery.

2.3 Copper extraction experiments

Large batches of CPT and SOR slurries were prepared as above with three representative Fe:OC ratios, 1:0, 1:3, and 1:10 at a pH of 6. This pH was chosen as a common sediment pH and

the range at which Cu sorption was highest for all Fe:OC ratios. The slurries were washed and centrifuged twice with 10 mM NaNO₃ to remove remaining dissolved phase reagents and were not dried prior to experiments. An aliquot of slurry of known density and Cu concentration was added to a 15 mL polypropylene centrifuge tube to maintain a fixed Cu mass of 10 μ g in each experimental extraction in order to compare readily between precipitation materials. For the extractions, the slurry solution was mixed with either Ca²⁺, L-glycine, L-histidine, or citric acid at a Cu:extractant molar ratio of 1:20 with a background 10 mM NaNO₃ solution at pH 6. For pH desorption reactions, a background 10 mM NaNO₃ solution pre-adjusted to pH 4-6 was added to the slurry. Triplicates vials were rotated for 24 hours prior to filtration and analysis.

2.4 Material Characterization

To image the precipitates, 20 μ L subsamples of the washed CPT slurry solutions (1:0, 1:3 and 1:10 Fe:OC ratio) were left to dry, covered at room temperature, on carbon-coated gold TEM grids. Samples were examined first using a FEI Tecnai T12 TEM (120 kV), and later using a ultra-high resolution JEOL 2010 FasTEM (200kV) in conjunction with an energy dispersive x-ray spectroscopy (EDS) system to determine morphology, particle size, and elemental composition of the precipitates. A Scintag model XDS 1000 was used for x-ray diffraction measurements using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) with a step size of 0.02° in θ .

2.5 Aqueous phase dissolved organic carbon (DOC) and elemental analysis

DOC samples were measured on an Apollo 9000 TOC Analyzer (Teledyne Tekmar, Mason, OH). Calibration and quality control (QC) standards were prepared from potassium hydrogen phthalate (Ricca Chemical, Arlington, TX and Fisher Scientific, Waltham, MA, respectively). QC samples and continuous calibration verification standards were within 20 percent or better of expected values.

Dissolved Cu and Fe concentrations in the filtrates were measured on an Agilent 7700 inductively coupled plasma mass spectrometer (ICP-MS) with a helium collision cell. Samples were acidified with trace metal grade HNO₃ prior to analysis. Standards and QC checks were prepared from independent high purity standards (Spex-Certiprep, Metuchen, NJ and VHG Labs, Inc., Manchester, NH). Scandium was used as an internal standard. QC samples, internal standards and spike recoveries were within 10 percent or better of expected values.

3.0 Results and Discussion

3.1 TEM Images of Fe-OC precipitates

The ferrihydrite precipitation product decreases in particle size and morphology as OC addition increases. The formation of ferrihydrite was confirmed with XRD where the broad peaks at 35 and 64 °2θ suggest 2-line ferrihydrite formation (Figure S2). The ferrihydrite that formed during CPT with Cu in the absence of OC was grouped in aggregates of approximately 5 nm particles (Figure 1A). In the presence of OC, the Fe oxide nanoparticle sizes were difficult to ascertain, particularly at the 1:3 Fe:OC ratios, but the electron dense ferrihydrite particles were noticeably more variable and smaller at the 1:10 Fe:OC ratio (Figure 1B, C). The background C corrected EDS analysis confirmed the relative ratio of C:Fe increased from the 1:0 to the 1:10 Fe:OC samples (Figure S1). The observed variation in size was expected since Fe oxide aggregation and crystal growth is disrupted in the presence of OC (Eusterhues et al., 2008; Hiemstra and Riemsdijk, 2009; Pédrot et al., 2011). Decreases in Fe oxide particle size due to OC content have been observed in both laboratory and field studies (Perret et al., 2000; Eusterhues et al., 2008), and the decrease from 5 nm to 1 nm would result in an increase in Fe oxide surface area from about 300 m²/g to 1500 m²/g assuming spherical particles. In addition to increased surface areas, laboratory studies have also observed increasing defect sites, disorder

and changes in crystallinity as Fe:OC ratios and particle sizes decreased (Eusterhues et al., 2008; Cismasu et al., 2011; Henneberry et al., 2012). The differences in Fe oxide particle sizes with increasing OC content imply a difference in reactive surface area for Cu and OC binding to the Fe:OC aggregates.

3.2 Dissolved phase concentrations after CPT and SOR reactions

The Cu sorption to Fe oxides with no OC increased with increasing pH for both CPT and SOR products (Figure 2). The sorption edge occurs from about pH 4.5 to 6 as expected for Cu binding to ferrihydrite (Lund et al., 2008) and represents a commonly observed response of cation sorption to Fe oxides, a combination of both weak outer sphere interactions and strong inner sphere interactions. The CPT reaction under the same condition had a similar dissolved Cu curve, but with significantly lower dissolved Cu concentrations at pH 5 and 5.5. The 1.3-fold and 2.4-fold lower dissolved Cu at those pH levels was due to additional interactions that occurred during CPT. Similar studies with Pb have also found more efficient metal removal during CPT reactions than SOR due to the formation of additional metal binding sites, which could be a combination of trapped Cu and isomorphic substitutions as has been postulated by others for Pb, Cd or Zn (Davranche and Bollinger 2000; Lu et al., 2011) and Cu (Karthikeyan et al., 1997). The surface bound metals during Fe oxide growth could easily get trapped in interior cavities between Fe oxide crystals. Studies examining aging and growth of nanoparticulate goethite at pH 6 while exposed to different metal solutions at millimolar levels showed that quickly sorbing species such as Cu impeded the growth of nanoparticles due to surface passivation, while slowly sorbing species such as Hg and Zn did to a considerably less extent (Kim et al., 2008). Kim et al. (2008) also observed continued uptake of Cu over time suggesting structural incorporation of the metals as the particles grew in size. The observed higher

concentrations of dissolved Fe left in solution during CPT (Figure S3) also suggest a difference in the precipitated materials. The approximately 0.2 mg/L of dissolved Fe remaining in the SOR reaction at pH 4 (Figure S3) matches a K_{sp} of $-37.8 = \{(\text{Fe}^{3+}) \cdot (\text{OH}^-)^3\}$ (Schwertmann, 1991), whereas the CPT data suggests a slightly higher K_{sp} of -37.2 which could be due to generation of a more amorphous structure upon Cu substitution or trapping within the Fe oxide structure and likely has implications for Cu retention.

Upon the addition of 3 mg/L OC, the observed trend was still a decrease in dissolved Cu concentration as the pH increased, but while the CPT reaction showed additional Cu removal from solution across the pH range compared to the 1:0 Fe:OC CPT reaction, the SOR reaction actually showed less or not significantly different Cu removal compared to the 1:0 Fe:OC SOR reaction (Figure 2). The dissolved C concentration (Figure S4) as well as the precipitate mass (Figure S5) were not significantly different between CPT and SOR reactions at different pHs. That suggests there was no solid phase mass dependent difference in Cu sorption, and the difference was presumably due to differences in available binding sites. In the CPT reaction, the decrease in dissolved Cu remaining in the 1:0.5 relative to the 1:0 Fe:OC reaction was likely a result of both a decrease in particle size due to Fe oxide precipitation in the presence of OC, increasing ferrihydrite surface and internal binding sites, as well as the formation of ternary binding sites (Hesterberg et al., 2011). Previous work suggests that in Fe oxide, Cu, and fulvic acid sorption reactions, ternary complexes (oxide-Cu-FA) are most prevalent near pH 5, but at higher pH, the bulk of Cu is bound to Fe oxide (Weng et al., 2008). The most significant difference between 1:0 and 1:0.5 Fe:OC CPT reactions was observed at pH 5 where oxide-Cu-OC ternary phases would more easily form since all reactants were present during precipitation. On the other hand, the SOR reactions at 1:0.5 Fe:OC actually produced an increase in dissolved

Cu from pH 5.5 to 6.5 relative to the 1:0 Fe:OC reaction. This is contrary to the expectation that a 10-20% decrease in dissolved Cu from SOR reactions would be observed based on surface complexation modeling (Figure S6) due to a higher surface area Fe oxide generated. In the case of SOR, it is likely that the sorption of OC to Fe oxides prior to Cu addition resulted in blockage of the Fe oxide surface binding sites, limiting the formation of inner sphere and ternary complexes. Blockage and enhanced sorption of metals have both been observed depending on the availability of ligand sites on the sorbed OC (Davis and Leckie, 1978).

As additional organic matter was added (1:3 to 1:10 Fe:OC), decreasing Cu concentrations with increasing pH up to pH 5.5 were observed. At the same pH range, both CPT and SOR reactions showed up to a 60% decrease in dissolved Cu relative to higher Fe:OC ratio samples. While the Fe oxide particle size was getting smaller, the decrease in dissolved Cu was probably more a result of increased OC binding sites since the differences in dissolved Cu between CPT and SOR reactions decreased as the OC content increased. NICA-Donnan dissolved organic carbon models suggest that OC dominates Cu binding at the 1:3 to 1:10 Fe:OC ratios. At the pH range above 5.5, the dissolved Cu started increasing as OC content increased. This was due to the increasing solubility of OC chelated metals, both Cu complexes and Fe complexes (Figure 2, S3, S4) that limited both the precipitation and/or aggregation of Fe oxides and Cu sorption. The presence of OC resulted in much lower or no measurable solid precipitation formed at pH 6.5 and 7 for the 1:6 and 1:10 Fe:OC ratio solutions (Figure S5). At these lower Fe:OC ratios and at pH 6 and above, color differences in the solution were evident. Prior to filtering, solutions had a dark brown color, and filtrates had a light brown color, whereas typically precipitation product filtrates were clear. The dissolved Fe data for CPT was not significantly different from SOR (Figure S3) in this pH range which suggests that the presence of

Cu at the time of precipitation did not affect Fe oxide precipitation and aggregation. While OC plays a role in maintaining Fe in solution at low Fe:OC ratios, it is unclear in this case whether it was primarily chelated Fe ions or destabilization of small Fe oxide aggregates, although the darker solution color suggests the latter. Fe oxide aggregates smaller than $0.2\ \mu\text{m}$ may have passed through our filters and have been observed in Fe precipitation products in the presence of high OC by others (Gaffney et al., 2008). It may be that there was a shift to more colloidal Fe oxide particles in the filtrate at high pH as the OC content increased since Karlsson and Persson (Karlsson and Persson, 2012) found both to be present dependent on the Fe concentration, pH and OC content. However at lower OC concentrations, the change in Fe distribution between solid and aqueous phase was minor in the 1:3 Fe:OC reactions and minimal at higher Fe:OC ratio reactions since dissolved Fe concentrations remained low (Figure S3) and the solid precipitate mass did not significantly change across the pH range (Figure S5).

The formation of Fe oxides under different OC concentrations alters the abundance, aggregate structure and sorption reactions with Cu. Other controlled experiments that examined the impact of different ratios of Fe(II):OC on Fe oxide aggregate formation at pH 6.5 showed that aggregates changed from nearly all >0.2 micron with little dissolved OC present to 70% less than 0.2 micron and greater than $50\ \text{kDa}$ at a 1:20 Fe:OC ratio, presumably due to ligand binding inhibiting oxidation of Fe(II) or growth of Fe oxide aggregates (Gaffney et al., 2008). Measurements of BET surface area of Fe-OC coprecipitates decreased to very low values, $< 5\ \text{m}^2/\text{g}$, at high OC content (Eusterhues et al., 2008), however it is unclear how that alters the availability of sorption sites and interactions with other metals. Although smaller Fe oxide particle sizes should promote more metal sorption reactions on the surface, the coating with OC likely inhibited those specific interactions and Cu sorption became more a factor of OC content

than Fe oxide surface area. The changes in Fe-OC coprecipitate reactivity toward Cu binding at different Fe:OC ratios is likely due to a combination of accessible Fe oxide surface area, specific OC ligand interactions, and differences in reaction rates during precipitation.

3.3 Differences in Cu extraction between CPT and SOR solids

Copper release from solid phases was assessed using extractants of increasing specificity for Cu. Samples for extraction were initially prepared at pH 6 because they showed the maximum sorption at the different Fe:OC ratios and at this pH the mass of Cu and Fe in the prepared solid phase were nearly equal with just a variation in mass of OC. The extraction conditions were meant to mimic potential changes in the environment, in which already formed Fe-OC precipitates would be exposed to 1) a drop in pH as soils are saturated, 2) excess Ca^{2+} as an ion exchanger, 3) organic ligands with different affinities for Cu or Fe (Glycine: $\log \beta \text{CuL} = 8.56$, $\text{FeL} = 10.8$ at 25 °C or Histidine: $\log \beta \text{CuL} = 10.6$, $\text{FeL} = 4.17$; Motekaitis, 2004), or 4) citric acid as a ligand and to reduce and dissolve Fe oxides (Waite and Morel, 1984; DiPalma and Mecozzi, 2007). The organic ligands with different stability constants were meant to observe the different effects of ligand strength on extraction of Cu from the solid phase as well as discern any differences in the presence of organic matter chelated Fe present in the solids.

The drop in sample pH typically resulted in increased dissolved Cu concentrations from CPT reactions relative to SOR reactions (Figure 3). In the case of no OC during CPT, the % Cu extracted increased from about 5% to 10% as the pH decreased from 6 to 4, but during SOR, there was no significant change. During CPT, Cu may have been bound in weaker binding sites relative to SOR due to the more amorphous structure of CPT products as suggested above. When the particles disaggregated to some extent when the pH dropped, possibly causing the small increase in dissolved Fe during CPT relative to no difference in SOR (Figure S7), more of

the weakly bound Cu was released. Formation of smaller aggregates has been shown for Fe oxide nanoparticles as pH drops (Baalousha et al., 2008). At the 1:3 Fe:OC ratio, the % Cu extracted increased with the decrease of pH for both CPT and SOR samples (Figure 3), but in this case were typically higher in the SOR samples, with the exception of the pH 4 sample. The difference in dissolved Cu after the precipitation reactions at low pH (Figure 2) followed the same trends, with dissolved Cu higher during CPT relative to SOR at pH 4, but lower than SOR at higher pHs. At even higher OC content (1:10 Fe:OC), the trend was reversed, and the % Cu extracted decreased in the CPT reactions with the exception of pH 4, while for SOR samples, the % Cu extracted still increased as pH was lowered. Any solubilized OC during resuspension that sorbed to the solid phase as pH decreased could explain the general decrease in both Cu and Fe in the CPT reaction. In both the 1:3 and 1:10 Fe:OC samples, there were increasing amounts of OC and therefore increased binding sites for Cu, and in particular more sites with higher binding affinities (Martinez-Villegas and Martinez, 2008), making them not directly comparable.

Chemical extractants have a greater effectiveness for increasing dissolved Cu in CPT than SOR products (Figure 4). Generally, as the strength of the exchange reaction increased, i.e. Ca displacing weakly bound Cu, and the use of ligands with increasing metal stability constants for Cu, the % Cu extracted increased. However, none of the extractions were significantly different in the 1:0 Fe:OC ratio SOR samples. We had expected that SOR products would release more Cu than CPT products due to its presence in the outermost layers of the solid, i.e. not in isomorphic substitutions, occlusions, and likely in fewer inner sphere complexes located on the surface. However, % Cu extracted was always higher for 1:0 Fe:OC CPT samples compared to SOR, but only in the case of histidine and citric acid were the % Cu extracted significantly different from the control. In the case of citric acid extractions, the solid Fe phase dissolved

significantly as well (Figure S8), and % Cu extracted was strongly correlated to dissolved Fe ($R = 0.99$, $p < 0.05$) across all the Fe:OC ratios. Citric acid promotes the Cu dissolution through both direct chelation of Cu and Fe, and dissolution of Fe oxides which could impact CPT products more (Waite and Morel, 1984; DiPalma and Mecozzi, 2007). During the reactions with citric acid, the solutions turned lighter in color, suggesting dissolution of Fe oxides was the dominant mechanism. Since both dissolved Cu and dissolved Fe were higher in the 1:0 Fe:OC CPT samples, it suggests the Fe particles were perhaps smaller or had more defect sites where citric acid could attack. This is consistent with the more amorphous structure in CPT reaction products as suggested above.

In the presence of OC, CPT reactions still showed higher % Cu extracted relative to SOR reactions. A higher proportion of the extractable Cu was likely bound to more OC sites in the SOR case, and since OC sites are typically higher affinity for Cu than Fe oxide sites, they would be less likely to exchange Cu (Martinez-Villegas and Martinez, 2008). For citric acid which promoted Fe dissolution, the % Cu extracted correlated strongly with % Fe extracted as above for the 1:0 Fe:OC samples. The only difference between 1:3 and 1:10 Fe:OC samples was the much higher % Cu extracted at 1:3 Fe:OC ratios. This could have been due to the presence of fewer Fe oxide surfaces and more chelated Fe and Cu at stronger sites within the organic matter in the 1:10 relative to the 1:3 Fe:OC ratio samples, limiting the available and more easily extracted metals. This could also explain the lower % Fe and therefore % Cu extracted in the 1:10 Fe:OC citric acid extracted samples, as citric acid couldn't extract metals bound to OC binding sites as effectively (Figure S8).

3.4 Environmental Implications

The coprecipitation of organic matter with ferrihydrite is common in wetland soils, but modeling the partitioning between solid and aqueous components and among solid phase sorption sites is not straightforward. Current equilibrium models for sorption to iron oxides or organic matter are based on either specific reaction stoichiometries or empirically determined thermodynamic constants (Goldberg 2013; Tipping 2004). These are effective for modeling metal sorption to each phase independently, but the assumption of additivity when modeling the ternary coprecipitation products is not always appropriate. In the comparison of CPT and SOR products even without OC, the route of precipitation product formation makes a difference e.g. producing trapped or isomorphically substituted Cu (Figure 2), which would result in an underestimation of sorbed Cu in the models. As Cu concentrations decrease in the environment, the contribution of the internal ferrihydrite sites to solid phase partitioning would likely be less important. More importantly, the organic matter likely plays a larger role in controlling Cu partitioning. . In particular, the largest differences in sorption were observed with low OC content where humic acid material inhibited Cu partitioning to the solid phase in SOR products, while enhancing it in CPT products. The model results of Cu sorption to ferrihydrite and organic matter falls in between the dissolved Cu observed in the SOR and CPT products at pH 5 and above, while dissolved Cu is underestimated below pH 5 (Figure S6). We assumed a ferrihydrite surface area of 300 m²/g and do not expect that differed between the SOR and CPT products at the same Fe:OC molar ratio. Therefore, we expect the difference between modeled and observed Cu concentrations are due to either blockage of Cu binding sites by OC in the case of SOR, or additional Cu forms (e.g. isomorphic substitutions, trapping of Cu or enhanced binding by OC) in the case of CPT as discussed above. At lower pH, the model suggests humic acid is the dominant binding phase, and the lower than expected Cu sorption may be due to differences in

the OC used in this study. In real sediments, further complexity exists with changes in ionic strength, competing cations, and variations in organic matter size and functional groups that could alter the final coprecipitate product and Cu binding.

Further analysis and modeling would benefit from isolating the size effects of ferrihydrite particles and specific OC interactions through the use of advanced spectroscopy techniques to independently measure Cu binding environments, but are often limited by high Cu detection limits. While in some Fe:OC molar ratios discussed above net Cu sorption was similar regardless of the Fe oxide-organic matter coprecipitate formation process, the availability of Cu from the solid phase was often quite different. In CPT products of Fe and OC, the form most likely formed in the environment, Cu was often more available. This difference in extraction suggests a difference in physical and/or chemical form dependent on the route of precipitate formation and ratio of Fe:OC. In natural environments, Cu availability from these phases may be higher than expected based on current models. Researchers conducting binding or exposure experiments should consider these differences in the solid phases used.

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473 Figure 1: Transmission electron microscopy images of coprecipitation reaction solids at 1:0

474 Fe:OC (A) on standard TEM; 1:3 Fe:OC (B) and 1:10 Fe:OC (C) on high resolution TEM.

Figure 2: Dissolved Cu concentrations as a function of pH for varying Fe:OC molar ratios during coprecipitation and sorption reactions.

Figure 3. pH induced desorption of Cu from varying Fe:OC ratio coprecipitation (A) or sorption (B) reaction solids. The solid phase Cu concentrations were kept constant for each Fe:OC molar ratio.

Figure 4: Extraction of Cu by various ligands or ions from varying Fe:OC molar ratio coprecipitation (A) or sorption (B) reaction solids. The solid phase Cu concentrations were kept constant for each Fe:OC molar ratio.