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Iron Oxide-Organic Matter Coprecipitates and Controls on Copper Availability

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Iron Oxide-Organic Matter Coprecipitates and Controls on Copper Availability

Neila N. Seda

B.S., Iowa State University, 2012

A Thesis

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

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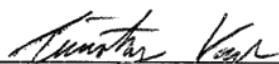
Masters of Science Thesis

Iron Oxide-Organic Matter Coprecipitates and Controls on Copper Availability

Presented by

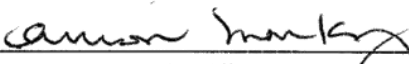
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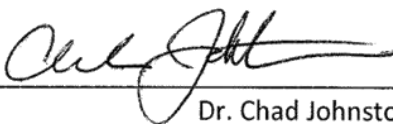
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Abstract

Copper availability in wetland systems is controlled by strong interactions with organic matter (OM) and highly sorptive mineral precipitates, such as iron oxides. The purpose of this study is to examine copper sorption and availability by using bench scale experiments to mimic more complex geochemical systems involving iron oxide and OM. Copper, iron oxide and OM coprecipitates were prepared by varying the molar ratio of Fe:OM from 1:0 to 1:10 with a fixed Cu concentration of 1 mg/L Cu, background of 10 mM NaNO_3 , and a pH range of 4 to 7. Precipitate mass and Cu sorption per mass were calculated by difference based on a mass balance. We found that as the ratio of Fe:OM decreased, more Cu was removed from solution. While solids at pH lower than 5.5 showed an increase of precipitated Cu for all Fe:OM ratios, at pH higher than 5.5 and higher Fe:OM ratios, increasing Cu remained in solution. Additional samples were prepared with Cu added after precipitation (sorption) to compare the in-situ conditions (coprecipitation) to conditions typically studied in laboratories and similar trends were observed. Iron oxide-OM coprecipitates exposed to Cu at the time of precipitation produced an increase in Cu removal from solution when compared to those for which Cu was added after precipitation. Ligand extractions, ion exchange reactions and desorption experiments consistently showed a clear increase in dissolved Cu material in the coprecipitation experiments when compared to sorption for all ratios. This may indicate that Cu is more accessible when considering multicomponent systems including Cu complexed with freshly precipitated iron oxide-organic matter coprecipitates.

1. Introduction

1.1. Copper fate and transport in dynamic systems

Copper is considered a high-profile pollutant in aquatic environments causing acute and chronic toxicity at levels as low as 13 µg/L and 4.8 µg/L, respectively (EPA, 2007). However, Cu is also a vital micronutrient for living organisms and is essential for many enzymatic processes. Dissolved Cu in the form of $\text{Cu}^{2+} \cdot 6\text{H}_2\text{O}$ is more bioavailable and therefore more toxic at low concentrations. However, Cu is rarely present in its fully hydrated form since it strongly binds to organic matter (Cabaniss et al., 1987). In addition, in soils with high redox cycling, more complex interactions of organic matter and Cu with metal oxides may further influence fate and transport.

1.1.1. *Cu retention and release in wetland systems*

The mobility, release and availability of metals is of great concern in aquatic systems such as streams and associated riparian areas or wetlands (EPA, 2007). Riparian zones or wetlands are mineral-rich transition areas important for water quality improvements, flood mitigation, and non-point source pollution management due to their high metal retention and biomass accumulation (Zhang et al., in review). While some studies have found total metal removal rates in constructed wetlands to reach up to 99% removal (Kadlec et al., 2008), others have observed –41% removal, meaning that net mass outflow is higher than inflow (Kadlec et al., 2008; Zhang et al., in review; Carleton et al., 2000; Hier, 2007), but the conditions that control retention or release are uncertain. In wetland systems, stable phases of Cu in the oxic surface water and top sediment layers are mostly species sorbed to organic matter or iron oxides, with dissolved Cu concentrations ranging from <1 nM to 2000 nM (Glass et al., 2012).

Oxidizing conditions are important for trace metal stabilization by processes such as adsorption, co-precipitation, or plant uptake (Grybos et al., 2007; Kadlec et al., 2008). In the reduced sediment environments, Cu can form stable sulfide minerals. As the wetland wets or dries and as concentrations of electron acceptors such as nitrate, iron or sulfate change, the location of the oxic-anoxic interface shifts, and microbial processes such as denitrification and iron reduction result in changes to the physical-chemical environment in terms of pH, redox, or organic matter cycling. These processes result in release of adsorbed metals and organic matter as iron oxides are reduced (Zhang et al., in review) or a release of organic matter as pH changes (Grybos et al., 2009) in the sediments (Carleton et al., 2000). Since residence times in wetlands are quite long, it is likely that input speciation of metals, which is typically as fine particulates or dissolved species (Hier, 2007), does not matter as much as changes within the wetland. In a recent case, most of the Cu in effluent was dissolved, and up to 60% of the dissolved Cu was observed associated with both Fe and organic matter colloids (Zhang et al., in review). In addition, the form of metal released may alter its fate and transport in receiving waters, e.g. promoting long range transport attached to an iron colloid. In the geochemically dynamic environment of a wetland soil where redox cycling stimulates recurrent uptake and release of iron and organic matter, Cu dynamics in particular are uncertain as these three components strongly interact. Also, as metals build up in riparian and wetland areas and as the frequency of rain events shift with climate change, there is more concern over release (Grybos et al 2009; Olivier-Lauquet et al., 2001; Zhang in review).

1.1.2. Cu fate coupled to redox cycling in wetland systems

In wetland sediments there are three distinct zones with respect to iron cycling: an oxic layer, an anoxic layer and an oxic-anoxic interface [(Salomons et al., 1987); Figure 1]. In the anoxic layer, microbial iron reduction occurs, releasing Fe(II) into the water column. As the iron travels up in the sediment to the oxic-anoxic interface, Fe (II) oxidation is rate limited by oxygen availability, until finally in the oxic surface water, iron rapidly hydrolyzes to ferrihydrite with some kinetic control based on pH. Organic matter dynamics also change as a result of iron cycling. Rapid cycling of iron in sediments has been shown to preserve organic matter due to sorption, but the characteristics of the organic matter removed are unclear (Lalonde et al., 2012; Riedel et al., 2013). Organic matter can sorb onto iron oxide surfaces and be released as iron is reduced, or interact with Fe as iron oxides precipitate, which has been shown to inhibit the conversion of ferrihydrite to goethite (Henneberry et al., 2012). Dissolved organic matter is also strongly associated with metals such as Cu which influences Cu retention and release. Field observations have noted release of Cu from wetlands correlated to iron, organic matter, or both in a variety of environments (Biasioli et al., 2010; Olivie-Lauquet et al., 1999; Zhang et al., in review). Previous research has indicated a transition from Cu correlated to iron, to correlations between both organic matter and iron in effluent from a local wetland as a storm event passed through (Zhang et al., in review). The specifics related to metal retention, release and availability from ternary Fe, OM and Cu phases is unclear.

In addition, the kinetics of these processes are important as there is likely competition for resources such as DOC, Cu, or Fe as microorganisms compete with

rapid chemical processes (e.g. iron hydrolysis at higher pH) or diffusion limited processes (e.g. migration of Cu between sorption sites). Moreover, the location of the oxic-anoxic interface is subject to change in space and time depending on flow events or water tables (Du Laing et al., 2007). These redox processes may result in higher dissolved ion concentrations such as Fe(II) or S^{2-} , shifts in pH, changes in mineral phase size and form, or changes to sorption products. Thus, the redox stability of iron oxides and the different geochemical processes in these zones is considered to be a major parameter regulating trace metal mobility and bioavailability in wetland soils (Grybos et al., 2007).

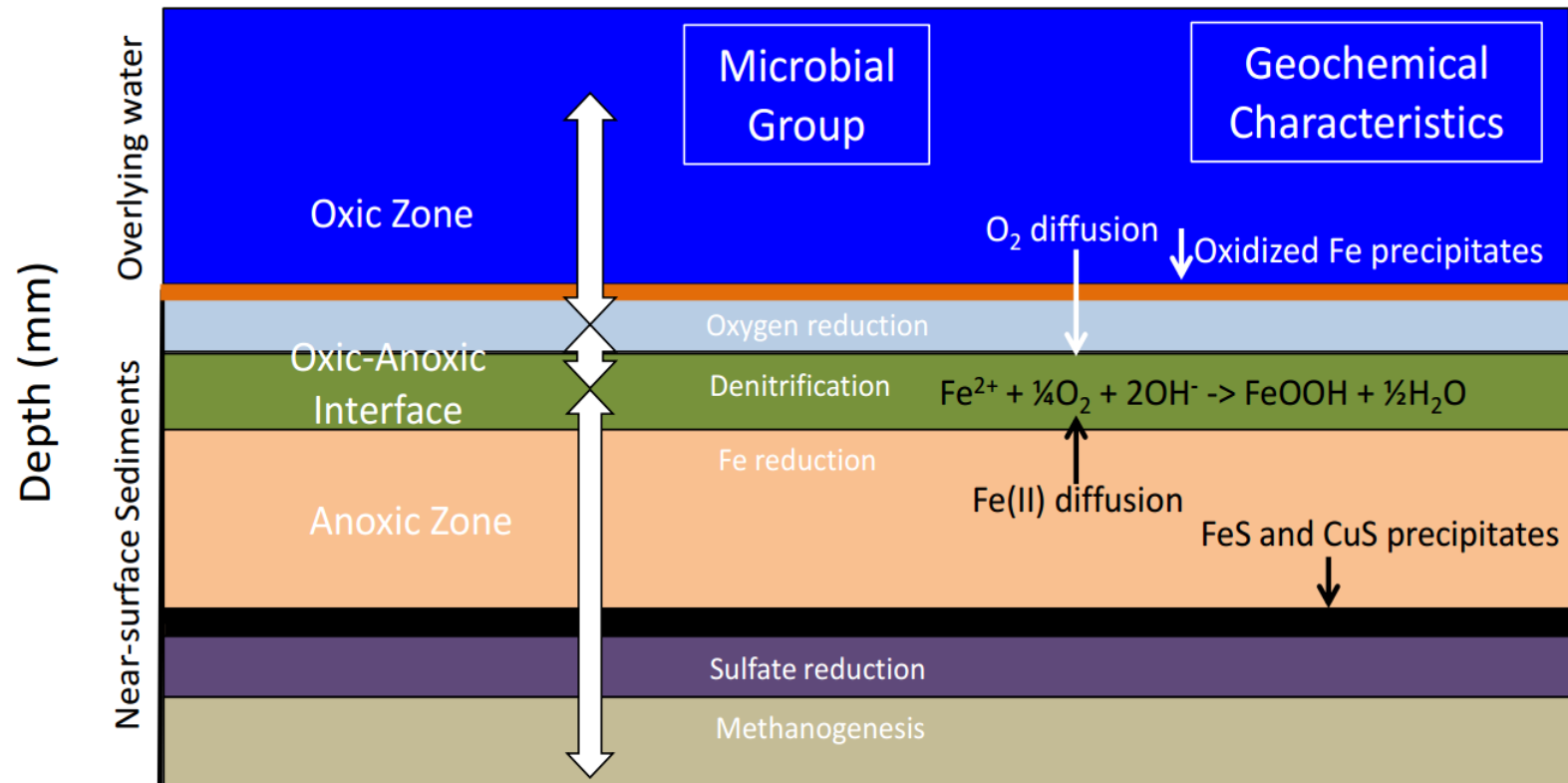


Figure 1. Sediment redox zones, microbial processes and major geochemical characteristics

1.2. Solid precipitate phase formation and interactions

1.2.1. Ferrihydrite formation and Cu interactions

Ferrihydrite (Fh) is an abundant, nanocrystalline Fe (III) oxyhydroxide mineral that when freshly precipitated forms small (2-6 nm) nanoparticles resulting in a highly reactive surface area (Michel et al., 2007). The reactive surface of these nanoparticles is a result of their chemical nature including charged surfaces and ligand groups, a relatively high surface area to volume ratio, and, when compared to other iron oxides (e.g. goethite); greater site surface density (Grafe et al., 2002; Baukhalfa et al., 2007). Ferrihydrite in particular is known for regulating free metal and OM concentrations in water through adsorption and coprecipitation (Lai et al., 2002). Cu sorption has been shown to reach up to 5 mg/g_{iron oxide} (Mustafa et al., 2008; Boujelben et al., 2009), and even more in freshly precipitated iron oxides (Sheinost et al., 2001). Copper removal can be achieved through coprecipitation, which is the incorporation of Cu within the iron oxide structure. This reaction is pH dependent and could limit Cu bioavailability by removing significant quantities of it from water or the mineral surface (Baukhalfa et al., 2007).

1.2.2. Organic matter control on iron precipitation

Iron oxides are commonly used in water and wastewater treatment to enhance precipitation and coagulation of organic matter and metal contaminants. This process also often occurs in the natural environment when Fe (II) is transformed into insoluble Fe (III) and forms a non-crystalline floc which can sorb metals and OM, thus allowing the stabilization of some forms of OM against microbial degradation (Eusterhues et al.,

2011; Henneberry et al., 2012). The formation of Fh nanoparticles in the presence of organic matter (OM) changes the rate of precipitation and its morphology (Poulton et al., 2005). This is primarily due to surface complexation involving carboxyl and hydroxyl functional groups (Gu et al., 1996; Schwertmann et al., 2005) dominating its ion-binding properties which disturbs Fh crystal growth and leads to coprecipitation of Fh-OM with smaller iron nanoparticles and organic matter surrounding them (Hiemstra, 2009; Eusterhues et al., 2011). Some studies have found that the presence of coprecipitated OM strongly inhibits the reductive crystallization of iron oxide materials, preventing change into an ordered crystal (e.g. hematite, goethite) regardless of pH, Fe:OM ratio and type of reductant added (Henneberry et al., 2012). It is likely that coprecipitation with OM significantly alters the reactivity of ferrihydrite due to the formation of smaller particles, different crystal structure, magnetic order (Schwertmann et al., 2005) and OM occlusion during coprecipitation (Eusterhues et al., 2008). These differences in morphology and makeup of iron and OM based colloids have been observed in both bench-scale and field samples (Perret et al., 2000). In addition to iron oxides forming coprecipitates with organic matter, these oxides commonly precipitate in the presence of metals such as Cu which has a high affinity for both OM and Fe. Research has not yet described more complex interactions between Fe precipitation, OM, and Cu that occur in natural systems.

1.2.3. Ternary systems – Iron-organic matter-copper

Cu has been shown to easily bind to organic matter due to carboxylic, amine, hydroxyl, and sulfhydryl groups present which can displace the hydration shell of dissolved copper to form a stable chelated solid phase. Previous research has found

that Cu, when compared to others metals, shows higher complexation stability with dissolved organic matter (DOM). The mobility of Cu is increased in the presence of DOM due to the formation of soluble Cu-DOC complexes (Martinez-Villegas et al., 2007). On the other hand, under no or low DOM conditions, ferrihydrite has been shown to act as the dominant adsorbent of metals and in the presence of fulvic acids, Cu sorption onto ferrihydrite has been shown to increase due to its strong affinity to sorbed organic matter (Henneberry, 2012). Under reduced conditions in wetlands, studies have shown high metal release from iron oxides as well as release of large amounts of dissolved organic matter due to pH increases from reduction reactions (Grybos et al., 2007). These studies have also shown that Pb and Ni release was controlled by a combination of iron reduction and DOM release (Grybos et al., 2007) which seems to indicate a role of the interaction between Fe and OM.

It is likely that coprecipitated organic matter leads to variation in the iron oxide mineral surface properties and reactivity towards metals. In part, sorption may be limited by competition with other inorganic cations or organic matter blocking access to binding sites, or enhanced by the presence of bound organic matter resulting in additional binding sites or higher affinity binding sites (Christl et al., 2001; Sheinost et al., 2001; Larsen et al., 2001; Hiemstra et al., 2009; Henneberry, 2012). This may also lead to less accessible surface sites on iron oxides for Cu due to OM occlusion, where occlusion is defined as the obstruction of available binding sites. In a study conducted in a multicomponent system, iron oxide alone was found to be the least effective competitor for Cu retention, which was attributed to iron oxide site blockage by DOC and lower binding affinity (Martinez-Villegas et al., 2007). Iron oxides are likely to

complex with organic matter components at a higher affinity than with Cu. Additionally, multicomponent studies have found that the affinity of iron oxides for Cu is described by a $\log K_1^{\text{int}}=2.89$ (Dzombak et al., 1990) while the affinity of Cu for humic acid can be described by $\log K_{\text{Cu-bidentate}} = 6.2$ (Gustafsson et al., 2003). These values, although not strictly comparable, could suggest that, in the presence of organic matter, Cu is unlikely to bind to iron oxides due to its higher affinity to organic matter components (Martinez-Villegas et al., 2007). On the other hand, research has found that the sorption of negatively charged organics by positively charged iron oxides can increase the number of negatively charged surfaces, thus increasing Cu binding and retention by iron oxides (Vermeer et al., 1998). Unfortunately with the complexity of OM, it is difficult to develop an effective model of mineral surface binding. Additional multicomponent speciation modeling including fresh precipitation of iron oxide surface and ternary complexes is required to understand the available binding sites and affinities for Cu onto coprecipitated Fe-OM.

1.2.4. Cu binding sites and characteristics

Binding of both Cu and OM onto mineral surfaces has been shown to be pH dependent, and as pH conditions change in wetland soils, these newly formed complexes may desorb from the iron oxides. Studies have commonly observed higher retention and metal uptake by iron oxides during metal coprecipitation experiments when compared to adsorption experiments (Karthikeyan et al., 1997; Karthikeyan, 1999; Lu et al., 2011; Crawford et al., 1993), and significantly lower pH sorption edges (Waychunas et al., 1993; Karthikeyan et al., 1997). However, it is not clear if during coprecipitation in the presence of organic matter whether metals will partition as

strongly into the iron oxide phase, or remain primarily in solution and chelated to OM on the surface of iron oxides. Of the contaminant metals studied in coprecipitation experiments, Cu has an ionic radius most compatible to substitution into the octahedral sites of ferrihydrite. The type of adsorption mechanism and binding sites accessible to Cu have been found to greatly affect accessible metal concentrations which is why it is important to understand the differences between these mechanisms and how the organic matter and iron oxide complexes control Cu distribution and availability in the environment.

In this study, coprecipitation (CPT) is defined as the presence of a trace element (Cu) during formation of an iron oxide or mixed iron oxide-OM precipitate and sorption (SOR) as the addition of surface attachment of Cu to Fe-OM coprecipitates after precipitation. Copper can precipitate within the structure of ferrihydrite (Fe-(Cu)-OH coprecipitate), displacing a Fe atom by isomorphic substitution and possibly retarding the rate of ferrihydrite transformation (Boukhalfa, 2010; Figure 2). Cu can also bind to the surface of iron oxides forming either inner- or outer-sphere complexes. Outer-sphere complexes are rapid and reversible reactions created when electrostatic forces attract hydrated Cu ions to accumulate at the surface of the charged iron oxide surface. These complexes make Cu relatively mobile due to the likelihood of Cu being replaced or exchanged with other cations present in higher concentrations. Inner-sphere complex formation of a metal with iron oxides is also fast (Grossl et al., 1997) but instead involves ionic or covalently bonded Cu to the surface of the iron oxides which makes the metal relatively immobile and unaffected by cation exchange reactions. The total sorption from these inner-sphere complexes increases over time likely due to mass

transfer limitations to the interior, non-exchangeable, sorption sites of the iron oxide (Sheinost et al., 2001).

In the presence of OM, the interactions can be either weakly bound surface complexes or more stable complexes at interparticle bridging sites (Osterberg et al., 1999). Consequently, two ternary complexes can be defined: type A and type B. Type A ternary complexes form when Cu chelates with OM and serves as a bridging cation between the mineral and the organic components (Fe-(Cu)-OM). A type B ternary complex, (Fe-OM-(Cu)) coprecipitate, is a sorption mechanism similar to that of dissolved Cu(II)-organic complex but involves mineral-bound organic matter, where Cu is bound to functional groups of the organic matter which in turn is bound to the mineral surface (Hesterberg et al., 2011). These types of complexes do not seem to be strictly dominated by pH and do not follow the same binding properties as single component systems (Robertson et al., 1994). Molecular-scale studies have found that at low levels of adsorbed humic acid, Cu binding was mostly type A where Cu was bound to humic acid and goethite simultaneously, whereas at higher levels, Cu formed type B ternary complexes primarily with functional groups of humic acid (Alcacio et al., 2000). In addition, these studies have found Cu competition with iron oxides for humic acid binding sites. A representation of these sorption and coprecipitation mechanisms is shown in Figure 2. Complex formation between the metal and OM affects total metal, sorption and the type of sorption mechanism, and the binding sites accessible to Cu likely affect accessible metal concentrations.

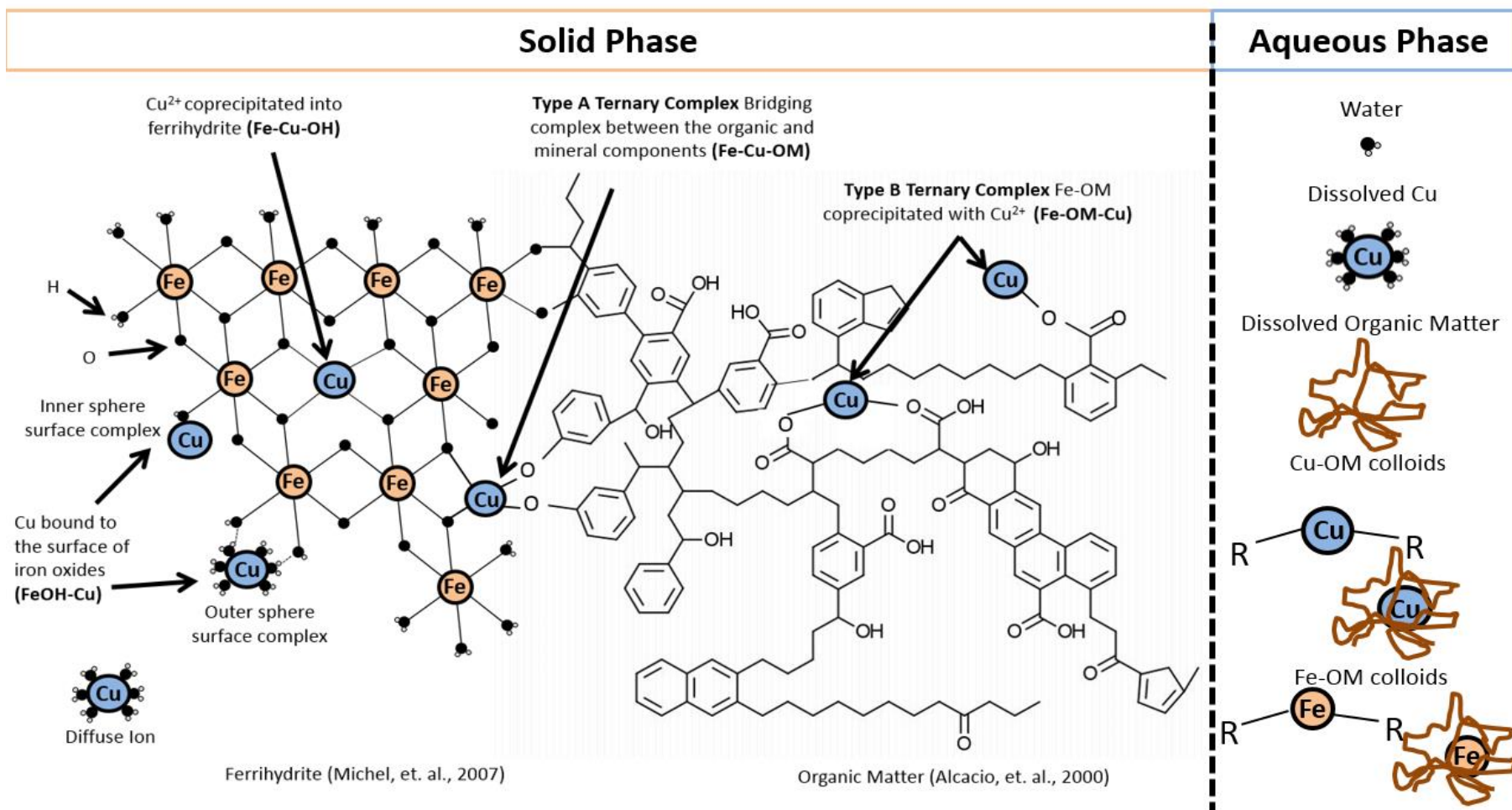


Figure 2. Visual representation of Cu binding sites on iron-oxide organic matter coprecipitates (Adapted from: Hesterberg et. al., 2011)

1.2.5. Controls on surface complexation

Complexation reactions are primarily dependent on (metal binding sites, iron oxide exchangeable and specific surface sites, pH, competing ion concentrations and organic ligands present). Organic matter has many functional groups that make up its extensive structure which are pH dependent and are responsible for the sorption of metals, being highest near neutral pH (McBride, 1994). These acidic functional groups can interact in various ways with iron oxides depending on their amount and position (Kaiser, 2003). An example of these are humic acids which have a pK_a value near 4 related to carboxyl groups and a pK_a value near 8 related to phenolate groups (Khan, 1973). Similarly, surface charge characteristics of mineral surfaces, such as the point of zero charge (PZC), influence various biogeochemical processes such as adsorption and desorption of ions, mineral dissolution and reactions with organic matter (Chorover et al., 2004). Iron oxides have pH dependent charged surfaces and specifically, ferrihydrite, has a point of zero charge of about 8 (Kosmulski, 2009), leading to a negatively charged surface at higher pH and a positively charged surface at lower pH. However, when ferrihydrite is coprecipitated with organic matter, the PZC value likely lowers as the surface is covered with organic matter that is primarily negative at a pH above 4 (Ketrot et al., 2013; Figure 3). Studies have found that OM can decrease the PZC of soil constituents up to ~1.0 units for every 1% increase in organic carbon (Anda et al., 2008) and in the case of goethite; the presence of 0.2 mg/L of humic acid lowered the net surface charge point from 9.1 to ~5.5 (Antelo et al., 2007). Under basic conditions, organic molecules become more electronegative and are likely to attract trace metals and positively charged surfaces. Also, at these conditions, other metals besides Fe start

precipitating as hydroxides. At higher pH values, iron oxides and OM repel each other as both become negatively charged and dissolved species are released into solution (Avena et al., 1998). Since Cu release seems to be dominated by iron oxides and organic matter, at higher pH we would expect higher concentrations of dissolved metals associated with OM and at lower pH for metal retention to be dominated by metal-organic complexes sorbed onto mineral surfaces (Grybos et al., 2007).

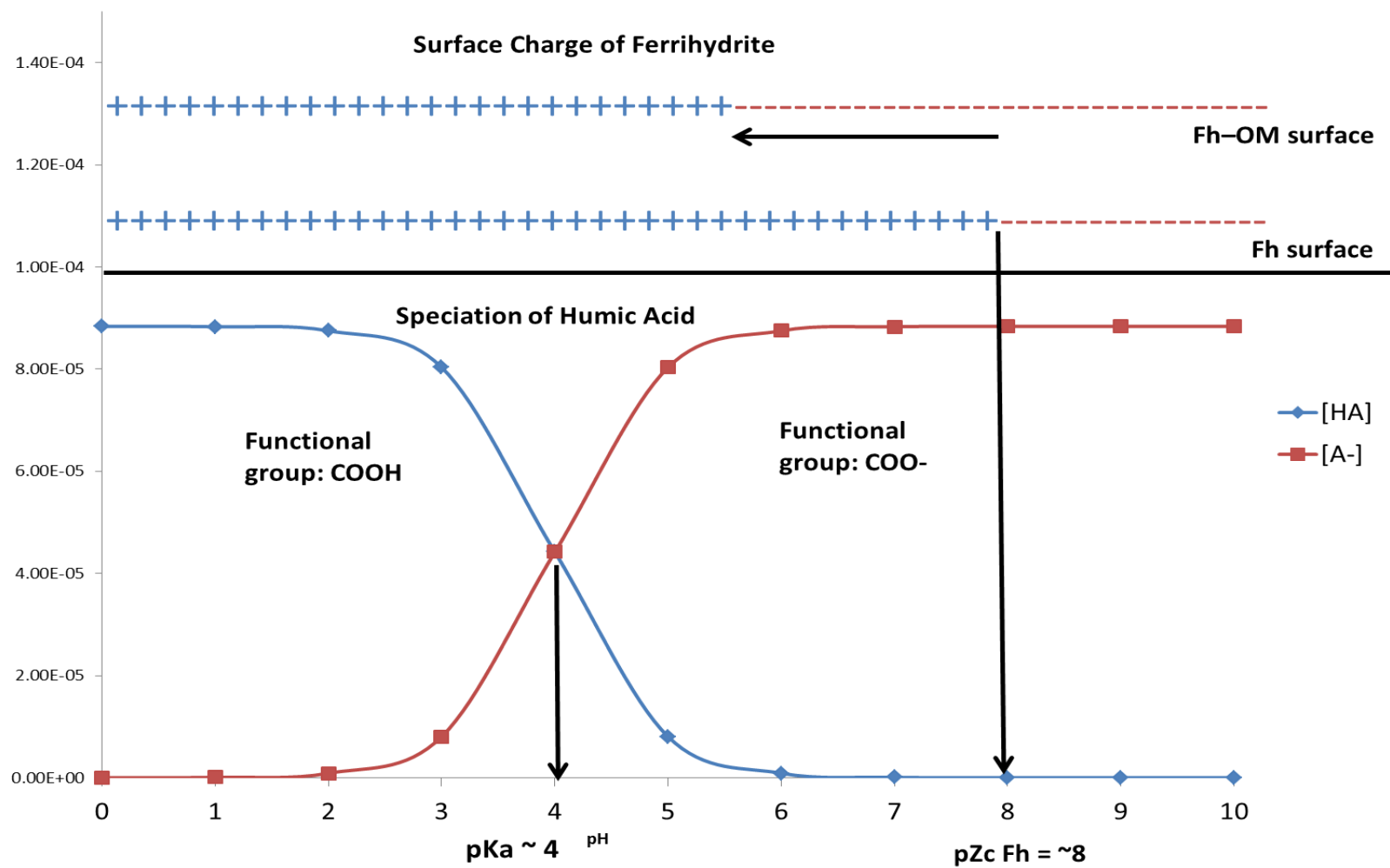


Figure 3. Representation of hypothesized influence of pH on speciation of OM and Fe-OH surface charge

1.3. Bioavailability

The mobility, behavior, and availability of trace metals is considerably influenced by processes like chelation, coprecipitation and sorption. Past research and modeling has focused on Cu sorption onto aged iron oxides individually as single-metal solutions in the presence of homogeneous solid phases to determine Cu partitioning and sorption rather than examining more complex systems (Boukhalfa, 2007). In most environmental systems, such as wetlands, multiple interactions occur simultaneously, including chelation of metals by dissolved organic matter, competition with other cations, such as Ca^{2+} , and a variety of sorption sites, continuous ferrihydrite mineral surface formation with different morphologies, varying redox and pH conditions and interactions of solid surfaces with complexing ligands and metals, Fe cycling and DOC. Disregarding these interactions may lead to significant inaccuracy in the estimation of metal mobility or bioavailability.

The speciation of metals in water, which depends on the water composition, is one of the main factors that controls availability and toxicity. Bioavailability is greatly affected by competing cations, ligand complexation and exchange to biotic ligands (US EPA, 2007). Free metals have been traditionally classified as the most important for uptake by the free ion activity model (FIAM) and the biotic ligand model (BLM), models that have been widely used for Cu control by organic matter. Available Cu is a concern to various organisms and at high concentrations can be lethal. The presence of dissolved organic carbon (DOC) in the water can prevent the toxic effects of Cu by creating complexes and making it less bioavailable. These models have been successfully applied in aquatic systems, particularly for Cu control by organic matter as

a function of pH and hardness. However, these models assume equilibrium and do not account for metal or organic matter interactions with mineral phases as an exchangeable phase. In a soil system with oxide phases, the control on bioavailability shifts from dissolved ligand lability at the smallest size (i.e. Cu-DOC) to a combination of ligand exchange, binding site strength, diffusion, and dissolution as Cu partitions to different phases. Truly dissolved phases of Cu are quite low in sediment environments, and the bulk of the labile Cu present may be in the colloidal phase. Differences of particle size within a colloidal aggregate may also play a role in limiting bioavailability, as smaller nanoparticles have a higher surface area to volume ratio which is more likely to bind Cu (Madden et al., 2006). However, in Fe-OM aggregates, this is in competition with potentially strong binding sites in OM as well, both of which may limit the exchange of Cu to organisms. In this research we are interested in understanding Cu availability in more complex geochemical systems including organic matter and ferrihydrite, and how it is affected by coprecipitation when compared to sorption.

1.4. Hypothesis and research objectives

Past metal release studies have focused on systems that include organic matter and/or metals on soils or aged iron oxides, but have not considered how coupled reactions between iron, Cu and OM during iron precipitation may affect metal retention or release. Understanding the retention capacity and dynamics of Fe-OM structures in terms of Cu is quite interesting, as each independent component (e.g. Fe oxide alone, or DOC alone) has a strong interaction with Cu. In this study, we first generate Fe-OM solid phases at different ratios of Fe:OM and with Cu added during (coprecipitation) or after (adsorption) precipitation. We expect CPT reactions to enhance Cu retention

compared to SOR. During coprecipitation reactions, more binding sites are available to Cu within the organic matter and the iron oxide, although they almost certainly have varying binding affinities. For the SOR reactions, the Cu is mostly bound to organic matter and is capable of accessing inner and outer sphere sites in the iron oxide structure. Cu availability was investigated by performing a series of ligand extractions with specific binding affinities to Cu, cation exchange and pH desorption reactions. At high Fe:OM ratios we expect Cu to be more available since the extractant is able to interact with the ferrihydrite surface. At lower Fe:OM ratios, ferrihydrite is mostly occluded by OM, which has a higher binding affinity for Cu, thus we expect extraction to be lower. Finally, we expect ligands with high binding affinities to be the most effective in Cu extractability.

2. Materials and methods

2.1 Reagent preparation

Stock solutions of NaNO_3 , $\text{Cu}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ were prepared from ACS grade reagents. To prevent precipitation of iron oxides, iron stocks were adjusted to pH of 2. Humic acid (Sigma Aldrich) stock was prepared by dissolution in water, followed by measuring dissolved carbon concentration with a TOC analyzer (see below) prior to use. Background Fe or Cu concentrations in all stocks were below detection. HA stocks were stored at 2°C. All solutions were made using 18 M Ω deionized water and containers were acid washed in 10% HNO_3 for 24 hours prior to use. Any pH adjustments in the following experiments were made using 0.01-1 M NaOH.

2.2. Bench scale coprecipitation (CPT) and sorption (SOR) reactions

Triplicate solutions of 50 mL of coprecipitation and sorption reactions were prepared in acid washed polyethylene bottles with five Fe:OM molar ratios varying from 1:0 to 1:10 and varying pH from 4 - 7 by addition of NaOH. CPT solutions were prepared in the following order with 10 mM NaNO_3 , Cu concentration fixed at 1 mg/L, HA added from 0 to 60 mg/L carbon, and Fe (added last) at a fixed concentration of 28 mg/L. SOR solutions were prepared following the same procedure, excluding the initial addition of Cu. The pH was adjusted to the experimental pH by dropwise addition of NaOH. Samples were then placed on a rotator at 30 rpm, 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. For SOR reactions, following iron

precipitation for 24 h in the presence of humic acid, Cu was added and the solutions were placed in the rotator for an additional 24 h to reach equilibrium. Following rotation, all samples were centrifuged at 3000 rpm for 30 min and vacuum filtered through a 0.22 μm filter paper (Millipore nitrocellulose membrane filter) in order to separate the solid-liquid mixture. The solid precipitate was placed in an oven at 75° C for 24 h and the dry mass was recorded. Filtrate samples were analyzed for Cu, Fe, and DOC concentrations as detailed below.

2.3. Solid phase partitioning of Cu

The mass of solid precipitate on the filter was weighed for each sample. Metal or carbon concentration in the solid phase was calculated by difference of the initial and final solution concentrations using the volume of reaction and the mass of solid precipitate as shown in Eq. 1.

$$Cs(\mu\text{g} / \text{g}) = \frac{([Cu]_o - [Cu]_f)(\mu\text{g} / \text{L}) * V_{\text{reaction}} (\text{L})}{M_{\text{solid}} (\text{g})} \quad (1)$$

Cs = μg of Cu per gram of total solid retained

$[Cu]_o$ = Initial concentration of Cu added

$[Cu]_f$ = Dissolved concentration of Cu measured by ICP-MS

V_{reaction} = total volume of precipitation = 50 mL

M_{solid} = dry mass of solid retained in filter paper

2.4. Copper slurry preparation for extractions

Large batches (1L solutions) of CPT and SOR solutions were prepared as above with three representative Fe:OM ratios, 1:0, 1:3, and 1:10 with the pH adjusted to 6. This pH was chosen as a common sediment pH and the range at which Cu sorption was highest for all Fe:OM ratios. Each batch was distributed into 20 acid washed 50 mL polypropylene centrifuge tubes and left to rotate for 24 hours at 30 rpm. After the 24 hours the CPT samples were centrifuged for 30 minutes at 3000 rpm, while the SOR samples were recombined into the 1L bottle in order to add an identical amount of Cu per sample, redistributed, and left to rotate for an additional 24 hours before centrifugation. One sample was sacrificed and filtered to measure Cu concentration to confirm solid phase concentrations. The remaining solid precipitates were washed once with 10 mM NaNO₃ at pH 6 and centrifuged again. The solid precipitates were combined into a total volume of 100 mL of 10 mM NaNO₃ pH 6 background solution as a uniform sample on which to perform extractions.

2.5. Copper extractions

Stock solutions of glycine, citric acid, L-Histidine (Figure 4), Ca²⁺ and 10 mM NaNO₃ background solutions at different pH (4, 4.5, 5, 5.5, and 6) were prepared for extractions. An aliquot of slurry of known density was added to all reactions in a 15 mL polypropylene centrifuge tube, so that the mass of Cu was fixed at a constant value for all experiments. For the ligand extractions, the slurry solution was mixed with either glycine, citric acid, L-Histidine, or Ca²⁺ at a mole-to-mole ratio of 1:20 (Cu:extractant) with a background NaNO₃ solution at pH 6. For pH desorption reactions, a background

NaNO₃ solution was added to the slurry at varying pH for each vial. Triplicates of these mixtures were left to rotate for 24 hours.

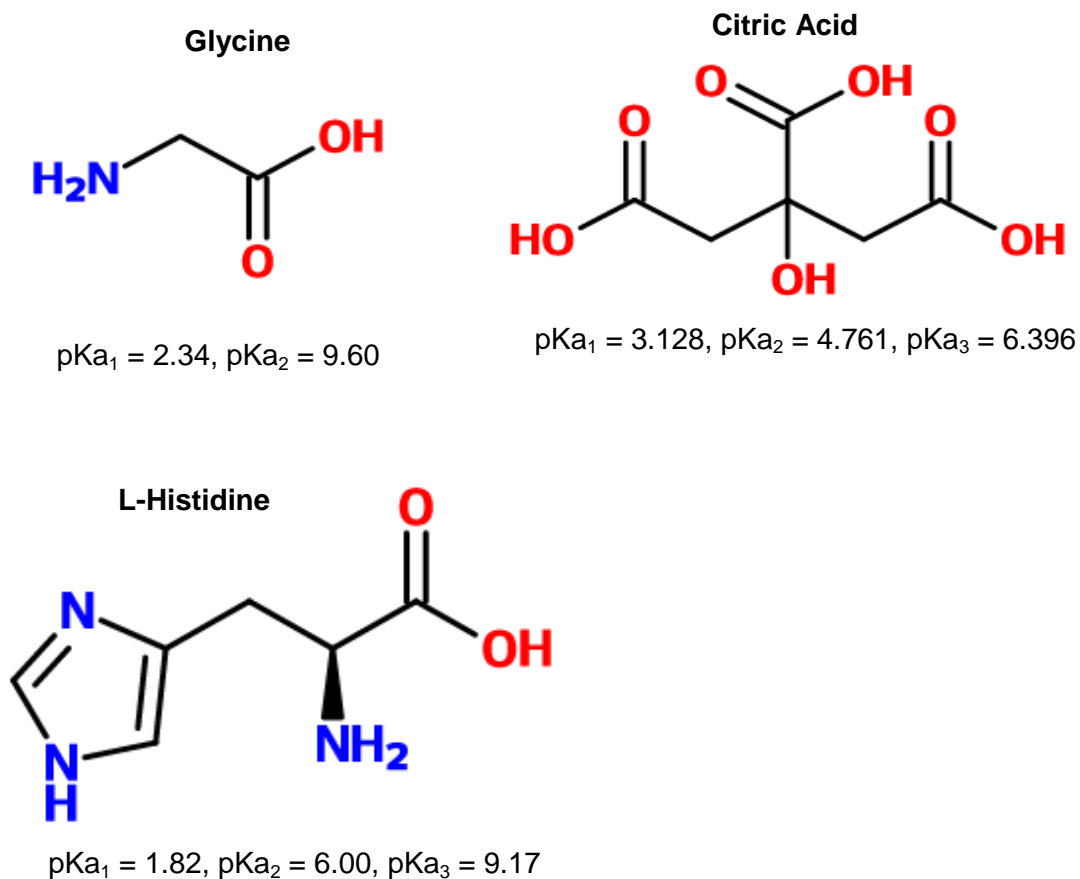


Figure 4: Ligand structure and properties for Cu extraction.

2.6. Sampling and analysis

2.6.1. Transmission Electron Microscope (TEM)

To image the fresh samples, 20 μL subsamples of the CPT slurry solutions (1:0, 1:3 and 1:10 Fe:OM ratio) were left to dry, covered at room temperature on carbon-coated gold grids. Samples were then examined first using a FEI Tecnai T12 TEM (120

kV), and later using a ultra-high resolution JEOL 2010 HRTEM (200kV) in conjunction with EDAX Genesis EDS (Energy Dispersive System) to determine morphology and particle size characteristics of the precipitates present.

2.6.2. Total organic carbon (TOC) analysis

DOC samples were measured on an Apollo 9000 TOC Analyzer (Teledyne Tekmar, Mason, OH) with a platinum oxidation catalyst. Potassium hydrogen phthalate was used for standards (Ricca Chemical, Arlington, TX), and laboratory prepared standards from the same chemical were used for quality control samples. QC samples and continuous calibration verification standards were within 20 percent or better of expected values.

2.6.3. *Inductively coupled plasma mass spectrometry (ICP-MS) analysis*

Total dissolved Cu and Fe concentrations in the filtrate solutions were measured on an Agilent 7700 ICP-MS with a helium collision cell. Samples were first acidified with trace metal grade HNO₃. The following instrument conditions were established: RF Power 1550 Watt, Nebulizer gas flow rate 1.05 L/min, nebulizer pump 0.1 rps, plasma gas 15 L/min Argon (Ar), carrier gas 0.77 L/min Ar, make-up gas 0.26 L/min. 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. Quality control samples, internal standards and spike recoveries were within 10 percent or better of expected values for ICP-MS measured elements.

3. Results and discussion

3.1. TEM Images of Fe-OM precipitates

TEM images were collected on the aggregate formed at pH 6 under different Fe:OM ratios. The ferrihydrite that formed during CPT with Cu in the absence of OM was grouped in aggregates of approximately 5 nm particles (Figure 5A and 5B). In the presence of humic acid, larger aggregates of Fe with OM were observed and iron nanoparticles were not as readily discernible on the standard TEM and therefore samples with OM were measured on the high resolution TEM. While the Fe nanoparticles were not quite as clear in the 1:3 Fe:OM ratio sample compared to the 1:10 sample, the sizes were approximately 3 nm and 1 nm, respectively. EDS confirmed the presence of Fe, Cu and C in all samples. There was some C content in all slides due to the layer of carbon support on the TEM grid, but the relative ratio of C:Fe in the EDX analysis increased from the 1:0 to the 1:10 Fe:OM samples. The observed variation in size was expected since iron oxide aggregation and crystal growth is disrupted in the presence of organic matter (Hiemstra, 2009; Eusterhues et al., 2011). Decreases in iron oxide particle size due to OM content have been observed in both laboratory and field studies (Eusterhues et al., 2011; Perret et al., 2000), and the decrease from 5 nm to 1 nm would result in an iron oxide surface area increase from about 300 m²/g to about 1500 m²/g. Recent lab-based studies have also observed increasing defect sites, disorder and changes in crystallinity as Fe:OM ratios and particle sizes decrease (Eusterhues et al., 2008; Cismasu et al., 2011; Henneberry et al., 2012). These differences in particle surfaces were expected to have an impact on metal binding to the Fe:OM aggregates.

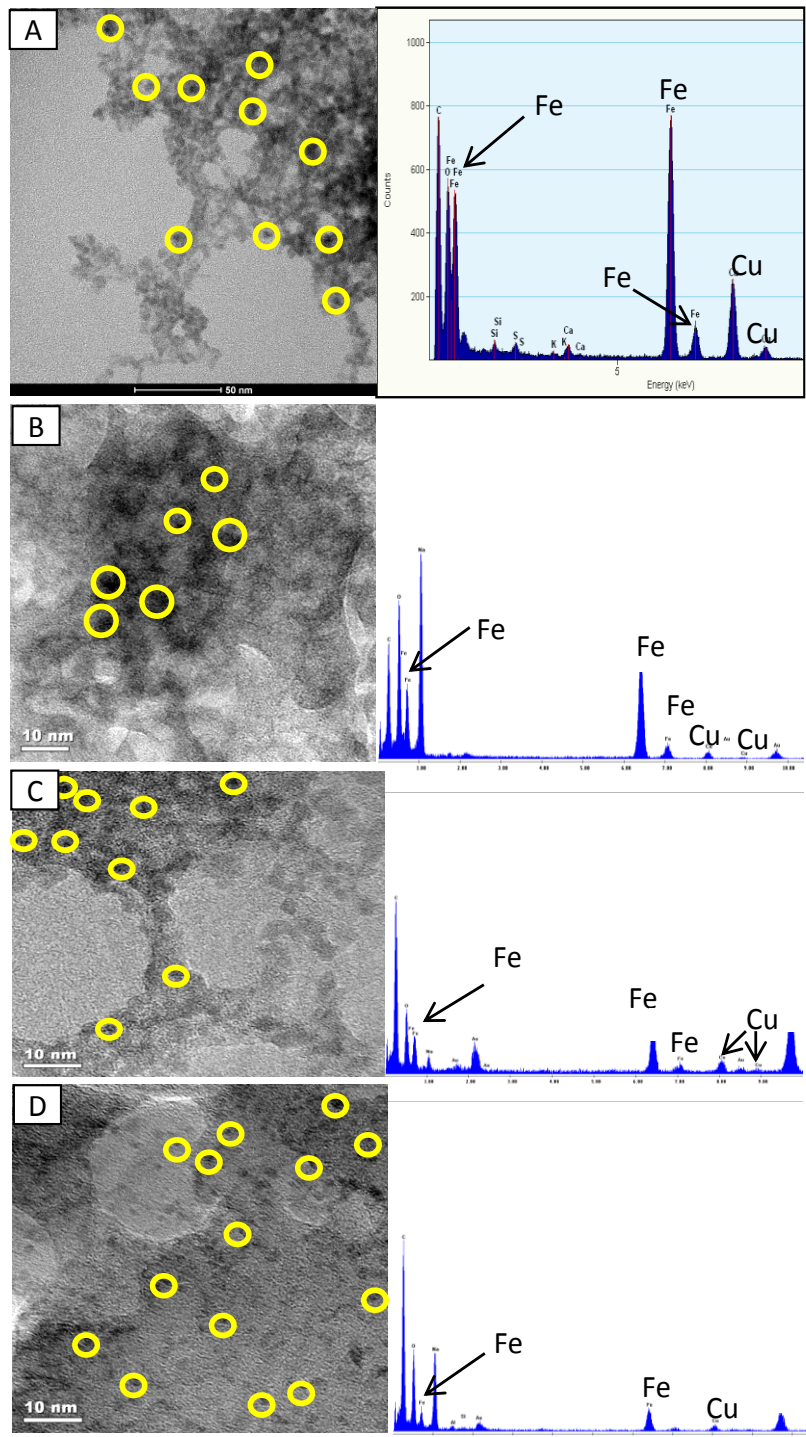


Figure 5: Coprecipitation TEM images of (A) 1:0 Fe:OM on standard TEM; (B) 1:0 Fe:OM, (C) 1:3 Fe:OM and (D) 1:10 Fe:OM on high resolution TEM. The 1:0 Fe:OM sample was subject to electromagnetic interference on the high resolution TEM. Yellow circles surround individual Fe oxide particles.

The formation of iron oxides under different circumstances has shown differences in both Fe aggregate formation and interaction with other metals due to specific ligand interactions, surface passivation and reactive surface area. On a bulk scale, controlled experiments that examined the impact of different ratios of Fe(II):DOC on iron oxide aggregate formation at pH 6.5 showed that aggregates changed from nearly all >0.2 micron with little DOC present to 70% less than 0.2 micron and greater than 50 kDa at a 1:20 Fe:OM ratio presumably due to ligand binding inhibiting oxidation of Fe(II) or growth of iron oxide aggregates (Gaffney et al., 2008). Although smaller particle sizes should promote more metal sorption reactions on the surface, the coating with OM likely inhibits those specific interactions. Measurements of BET surface area of Fe-OM coprecipitates decrease to very low values, $< 5 \text{ m}^2/\text{g}$, at high OM content (Eusterhues et al., 2008), however it is unclear how that alters the sorption sites and interactions with other metals. The changes in Fe-OM aggregate reactivity toward Cu binding at different Fe:OM ratios is likely due to a combination of accessible iron oxide surface area, specific OM ligand interactions, and reaction rates.

3.2. Solution phase concentrations after CPT and SOR reactions

Following each precipitation reaction, solution phase concentrations of Cu, DOC and Fe were measured and showed distinct differences between pH, Fe:OM ratios, and CPT and SOR reactions. The CPT reactions of Fe in the presence of Cu and no OM showed a decrease in dissolved Cu with increasing pH (Figure 6), with a large decrease between pH 4.5 and 6. The SOR reaction under the same condition had a similar shape of the dissolved Cu curve, but with higher dissolved Cu concentrations at pH 5 and 5.5. These two reactions represent a very commonly observed response of cation sorption

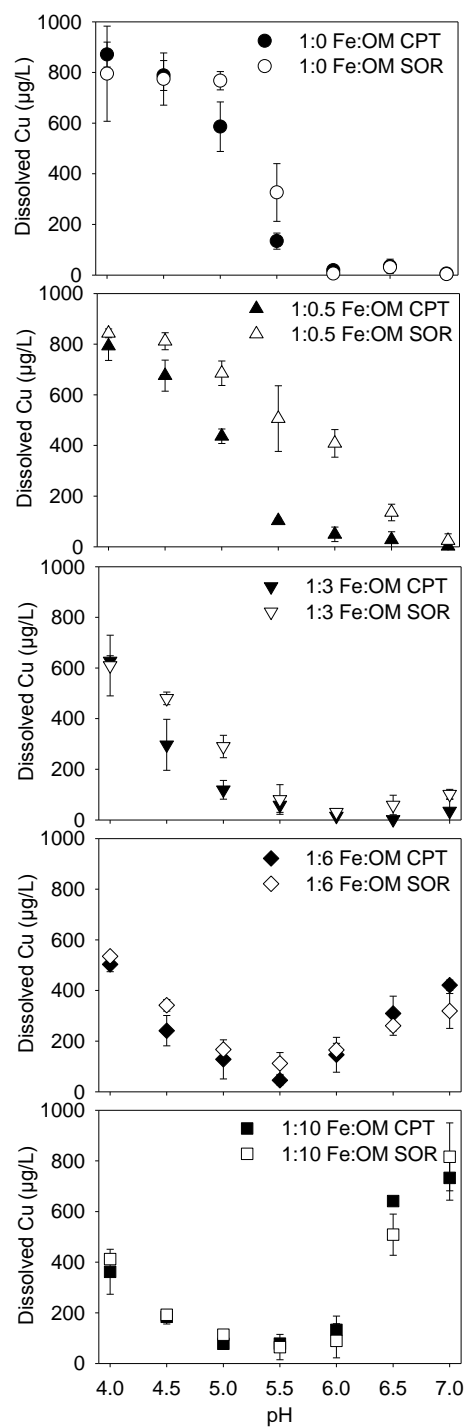


Figure 6. Dissolved copper concentrations as a function of pH for varying Fe:OM ratios during coprecipitation (CPT) and sorption (SOR) reactions. Initial copper concentration = 1000 µg/L

to iron oxides, a combination of both weak outer sphere interactions due to electrostatic attractions and more importantly strong inner sphere interactions due to the replacement of the hydration shell of the dissolved metal with one or two surface oxygen groups on the oxide. The 1.3-fold and 2.4-fold higher dissolved Cu during SOR at pH 5 and 5.5, respectively, was likely due to additional interactions that occurred during CPT. This could be due to a combination of isomorphic substitutions or occlusion of the Cu in interior cavities as the iron oxide particles aggregate and grow as has been observed experimentally for Pb (Lu et al., 2011) and Cu (Karthikayen et al., 1997). 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 As(V) and 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). The observed higher concentrations of dissolved Fe left in solution during CPT (Figure 7), most prominently at pH 4 where hydrolysis rates are already lower, was likely an artifact of the reduced growth rate in the presence of Cu. Kim et al. (2008) also observed continued uptake of Cu over time suggesting structural incorporation of the metals as the particles grew in size. Spectroscopic studies on Cu CPT with iron oxides have also observed Cu to retard the transformation of ferrihydrite to goethite at pH <8, and differences in desorption, X-ray diffraction and thermal analyses suggest Cu was both surface bound and incorporated inside the oxide structure (Boukhalfa et al., 2010). Similar studies have found CPT reactions with ferrihydrite to represent a greater binding strength than SOR due to the formation of additional metal binding sites. (Lu et al., 2011)

Upon the addition of OM, a more distinct difference was observed between CPT and SOR reactions at low OM concentrations. In the case of 1:0.5 Fe:OM ratios, the 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:OM CPT reaction, the SOR reaction actually showed less or not significantly different Cu removal compared to the 1:0 Fe OM SOR reaction (Figure 6). The dissolved C concentration (Figure 8) as well as the precipitate mass (Figure 9) were not significantly different between CPT and SOR reactions at different pHs. While that suggests there was no solid phase mass dependent difference in Cu sorption, the difference was presumably due to differences in available binding sites. In the CPT reaction, the decrease in dissolved Cu in the 1:0.5 relative to the 1:0 Fe:OM reaction was likely a result of both a decrease in particle size due to precipitation in the presence of OM, increasing ferrihydrite surface and internal binding sites, as well as the presence of OM binding or ternary Fe-OM-Cu or Fe-Cu-OM binding sites (Hesterberg et al., 2011). However, in the case of SOR, it is likely that the sorption of OM prior to Cu addition, resulted in blockage of the surface binding sites, limiting the formation of inner sphere and ternary complexes. Competition or enhanced sorption have both been observed depending on the availability of ligand sites on the sorbed OM (Davis and Leckie 1978).

As additional organic matter was added (1:3 to 1:10 Fe:OM), the same trends of decreasing Cu concentration with increasing pH, up to pH 5.5 were observed. At the same time, both CPT and SOR reactions showed decreasing concentrations of dissolved Cu as organic matter content increased. While the Fe oxide particle size was

getting smaller, the decrease in dissolved Cu was probably more a result of increased OM binding sites since the differences in dissolved Cu between CPT and SOR reactions decreased as the OM content increased. At the higher range of pH above 5.5, the dissolved Cu started increasing as OM content increased. This was due to the increasing solubility of OM chelated metals, both Cu complexes and Fe complexes that limited the precipitation or aggregation of Fe oxides and Cu sorption. This was corroborated by the increasing dissolved Fe and C concentrations (Figure 7, Figure 8) as OM content and pH increased. The presence of OM resulted in much lower or no measurable solid precipitation formed at pH 6.5 and 7 for the 1:6 and 1:10 Fe:OM ratio solutions. At these lower Fe:OM 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 filtrates were clear. The dissolved Fe data for CPT was not significantly different from SOR in this pH range which suggests that the presence of Cu at the time of precipitation did not affect iron oxide solid formation. The role of OM is more likely, as Fe oxide aggregates smaller than 0.2 μm have been observed in Fe precipitation products in the presence of high OM (Gaffney et al., 2008). While organic matter plays a role in maintaining iron in solution at low Fe:OM ratios, it is unclear in this case whether it was primarily chelated Fe ions or small iron oxide colloids. It may be that there was a shift to more colloidal iron oxide particles in the filtrate at high pH as the OM content decreased since Karlsson and Persson (2012) found both to be present dependent on the Fe concentration, pH and OM content. The change in distribution between solid and aqueous phase was minor in the 1:3 Fe:OM reactions and minimal at higher Fe:OM ratio reactions since dissolved Fe

concentrations remained low (Figure 7) and the solid precipitate mass did not significantly change across the pH range (Figure 9).

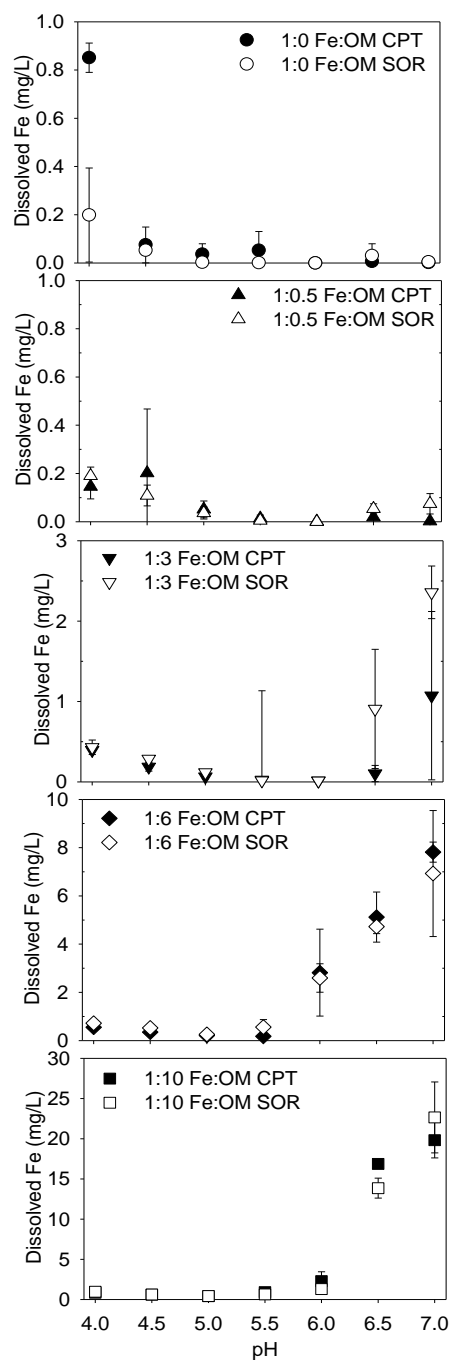


Figure 7. Dissolved iron concentrations as a function of pH for varying Fe:OM ratios during coprecipitation (CPT) and sorption (SOR) reactions. Initial iron concentration = 28 mg/L.

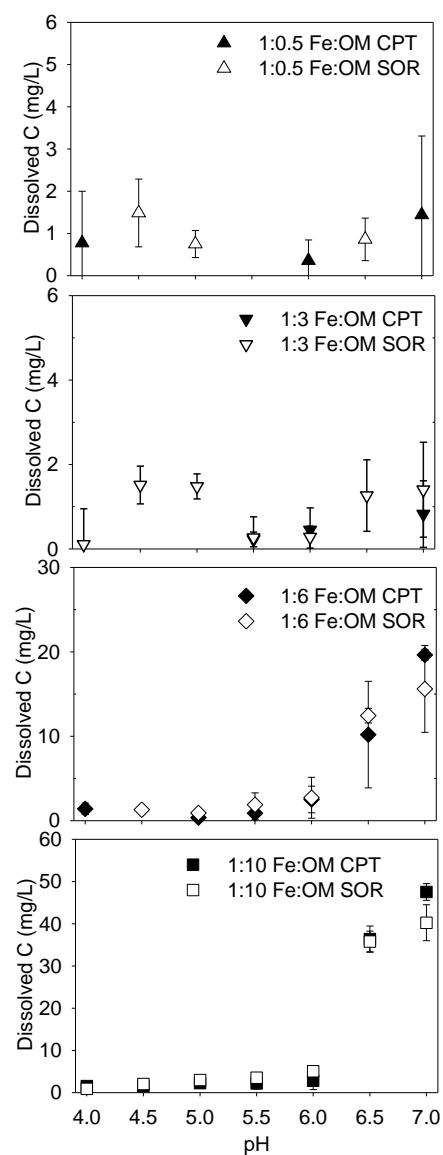


Figure 8. Dissolved C concentrations as a function of pH for varying Fe:OM ratios during coprecipitation (CPT) and sorption (SOR) reactions. Initial OM concentrations ranged from 3 mg/L in the 1:0.5 Fe:OM reaction to 60 mg/L in the 1:10 Fe:OM reaction.

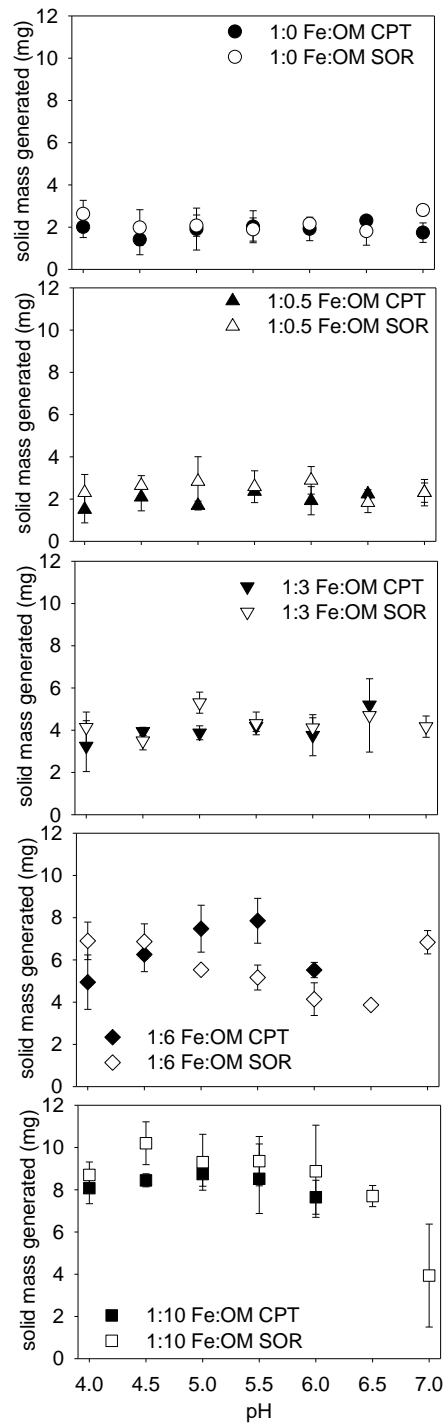


Figure 9: Mass of solid retained as a function of pH and varying Fe:OM ratio during coprecipitation (CPT) and sorption (SOR) reactions.

3.3. Extraction experiments for CPT and SOR solids

A variety of extractions to release Cu from the different solid phases were used to assess potential differences in Cu binding and strength. Samples for extraction were initially prepared at pH 6 because they showed the maximum sorption at the different Fe:OM 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 OM. The extraction conditions were meant to mimic potential changes in the field, in which already formed Fe-OM precipitates would be exposed to 1) a drop in pH as soils are saturated, 2) excess Ca^{2+} as an ion exchanger, 3) simple organic ligands with different affinity for Cu or Fe (Histidine: $\log \beta \text{ CuL} = 10.6$, $\text{FeL} = 4.17$; or Glycine: $\log \beta \text{ CuL} = 8.56$, $\text{FeL} = 10.8$ at 25 °C; Martel et al., 2009), or 4) citric acid to reduce and dissolve iron oxides ($\log \beta$ (25°C) $\text{FeL}=13.5$; Martel et al., 2009). Samples were established that kept Cu content in the solid phase constant.

The drop in sample pH typically resulted in increased dissolved Cu concentrations from CPT reactions relative to SOR reactions (Figure 10). In the case of no OM 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. The % Fe extracted increased in both reactions, though only by very small amounts (<0.5%), and the much larger increase in dissolved Cu could not be due to differences in Fe oxide dissolution. The difference could have been due to differences in the binding type and changes in physical state of the iron. During CPT, Cu may have been bound in weaker binding sites relative to SOR, and when the particles disaggregated to some extent when the pH dropped as has been shown for iron oxide nanoparticles (Baalousha et al.,

2008), more of the weakly bound Cu was released. At the 1:3 Fe:OM ratio, the % Cu extracted increased for both CPT and SOR samples (Figure 10), but were typically higher in the SOR case, with the exception of the pH 4 sample. Since humic acids tend to precipitate more as pH is lowered, the CPT samples likely became more compact and or larger aggregates, limiting accessibility to solution exchange. Though extractions are performed on washed products, the difference in dissolved Cu after the precipitation reactions at low pH (Figure 6) followed the same trends, with dissolved Cu higher during CPT at pH 4, but lower than SOR at higher pHs. At even higher OM content, the trend was reversed, and % Cu extracted decreased in the CPT reactions with the exception of pH 4, while for SOR samples, % Cu extracted still increased as pH was lowered. Any solubilized OM during resuspension sorbing to the solid phase as pH decreased could explain the general decrease in both Cu and Fe (Figure 11) in the CPT reaction. In both the 1:3 and 1:10 Fe:OM samples, there were increasing amounts of OM and therefore increased binding sites for Cu, making them not directly comparable. Also, since OM has a range of binding sites with different affinities (Hur et al., 2011), and the exchange rates are likely different, the differences in trends could be due to kinetic limitations.

Across the range of cation or ligand extractions, CPT products at all Fe:OM ratios showed higher % Cu extraction than SOR products, and the 1:3 Fe:OM ratio samples had the highest extractable Cu within each extraction type (Figure 12). 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 (glycine < citric acid < histidine) (Martel et al., 2009), the % Cu extracted increased within the 1:0 Fe:OM ratio CPT samples, while none of the extractions were significantly different in the 1:0 Fe:OM

ratio SOR samples. We had generally expected that SOR products would release more Cu due to its presence in the outermost layers of the solid, i.e. not in isomorphic substitutions, occlusions, and likely in fewer inner sphere and bridging type ternary complexes located on the surface. Only in the case of histidine and citric acid were the % Cu extracted significantly different from the control in the CPT samples. We don't expect there were large differences in the surface bound Cu binding sites because the Cu concentrations in the solid were at least two orders of magnitude lower than the sorption capacities of 2-5 mg/g observed by others (Boujelben et al., 2009), and it is unclear why histidine caused a small increase in extracted Cu for CPT. In the case of citric acid extractions, the solid Fe phase dissolved significantly as well (Figure 13), and % Cu extracted was strongly correlated to dissolved Fe ($R^2 = 0.98$) across all the Fe:OM ratios. Studies have found citric acid extraction of Cu to be minimal in sediments while, due to its strong affinity to citric acid, Fe dissolution was found to be high (above 39%) (Di Palma et al., 2007). Thus, citric acid likely impacts the dissolution of coprecipitated Cu through both direct chelation of Cu and Fe, and dissolution of Fe oxides. During the reactions with citric acid, the solutions turned lighter in color, suggesting dissolution of Fe oxides was a dominant mechanism. Since both dissolved Cu and dissolved Fe were higher in the 1:0 Fe:OM CPT samples when compared to SOR, it suggests that CPT samples were subject to faster dissolution rates or additional defect sites perhaps due to the metal interfering with Fe oxide aggregation as others have seen (Waychunas et al., 1993), though typically at much higher Cu concentrations relative to Fe (Kim et al. 2008).

In the presence of OM, CPT reactions still showed higher % Cu extracted relative to SOR reactions and in most cases, the % Cu extracted increased with the strength of the extractant. A higher proportion of the extractable Cu was likely bound to OM sites in the SOR case, and since OM sites are typically higher affinity for Cu than Fe oxide sites (Martinez-Villegas et al., 2008), they would be less likely to exchange Cu. For citric acid which promoted Fe dissolution, the % Cu extracted correlated strongly with %Fe extracted, as above for the 1:0 Fe:OM samples. The only difference between 1:3 and 1:10 Fe:OM samples was the much higher % Cu extracted at 1:3 Fe:OM ratios, which was likely due to the presence of more chelated Fe as opposed to Fe oxides in the 1:10 relative to the 1:3 Fe:OM ratio samples and could explain the lower % Fe and therefore % Cu extracted as citric acid couldn't compete well with OM binding sites.

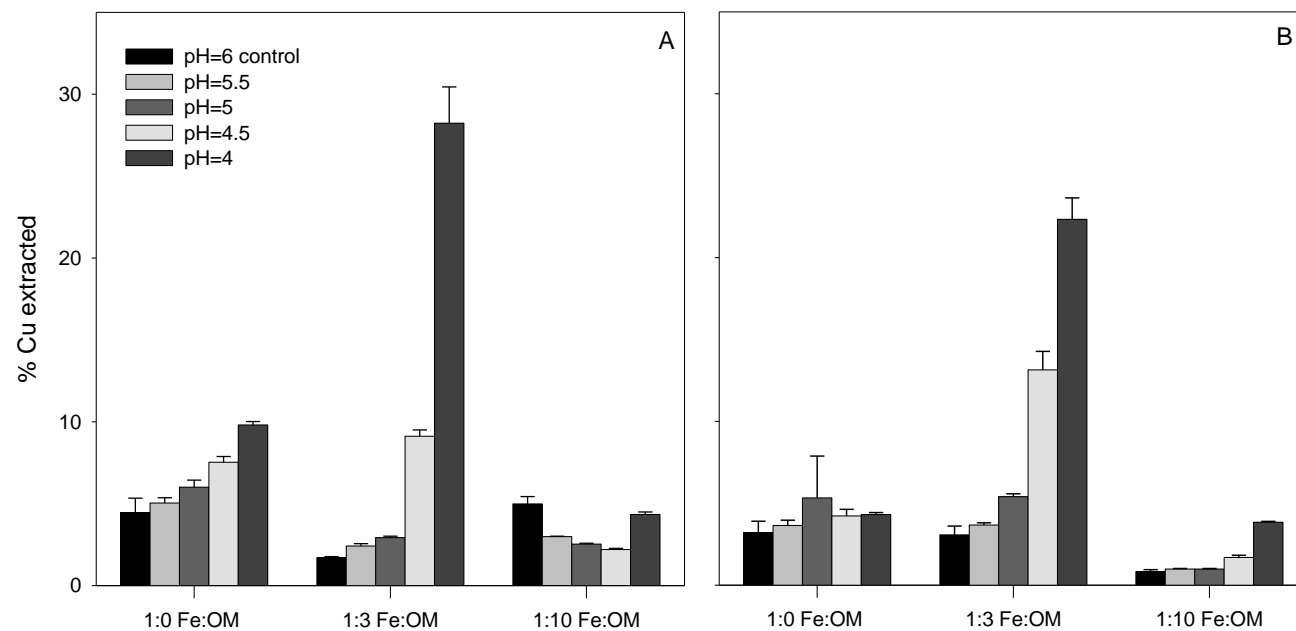


Figure 10. pH desorption of copper at varying Fe:OM ratios for (A) coprecipitation, and (B) sorption. Samples were normalized to Cu mass in the solid phase.

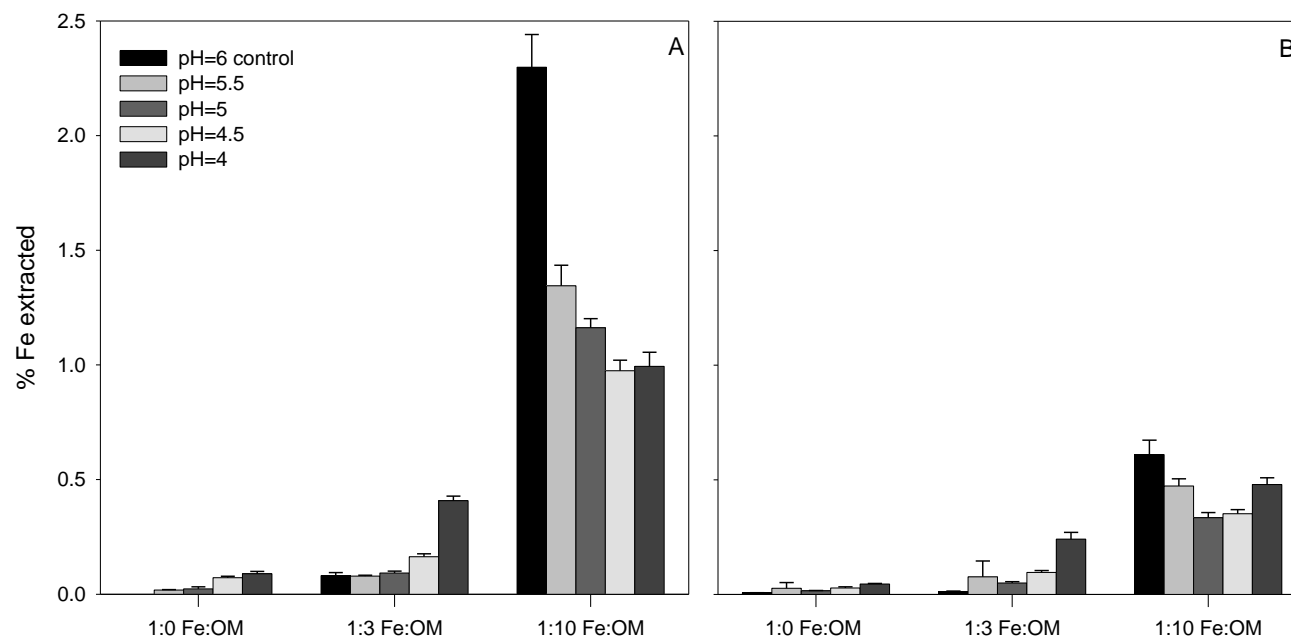


Figure 11. pH desorption of iron at varying Fe:OM ratios for (A) coprecipitation, (B) sorption

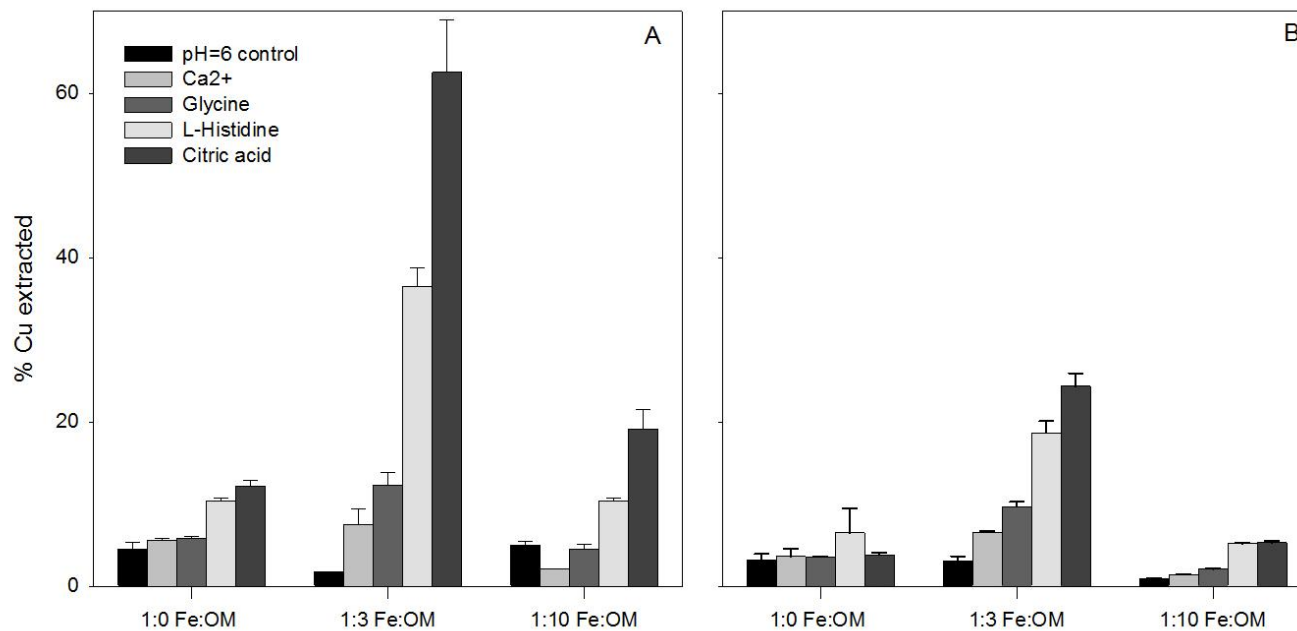


Figure 12. Extraction of copper by various ligands or ions at varying Fe:OM ratios, (C) coprecipitation, (D) sorption. Solid phase Cu concentrations were fixed between experiments. (A) shows the WHAM model for coprecipitated solids extraction and (B) for sorption solids.

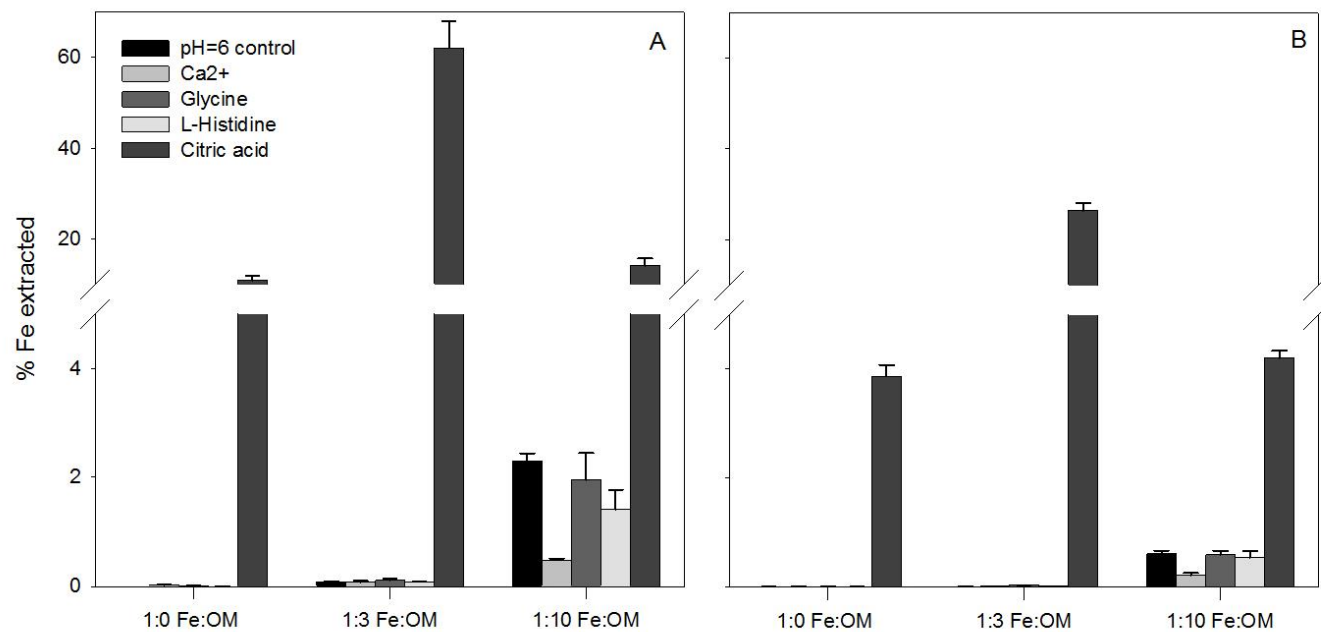


Figure 13. Ligand/Ion Exchange Extraction of iron at varying Fe:OM ratios for (A) coprecipitation, and (B) sorption.

4. Conclusion

The purpose of this study was to examine Cu retention and availability in more complex geochemical systems including highly sorptive species such as iron oxides and organic matter and to apply this knowledge to mineral-rich transition areas such as wetlands. For this, a multi-component system including Fe-OM-Cu phases was mimicked and dissolved data was collected for coprecipitation reactions, where Cu was added at the time of precipitation and sorption reactions, where Cu was added after precipitation. A series of extractions, consistently showed SOR reactions retained most of the Cu, release less dissolved Cu, when compared to CPT reactions, thus rejecting our initial hypothesis where we stated that CPT reactions enhanced Cu retention in the solid phase. Cu availability was highest for CPT reactions which may pose a great concern over toxicity to living organisms in these complex systems if the released concentrations of metal are high. Wetland systems, which are currently, used for water quality improvements due to their high metal retention properties, up to 99% in some instances, should be well monitored. As discussed before, these dynamic systems are affected by storm events and experience redox cycling which stimulates the recurrent uptake and release of Fe and OM which in turn affect available Cu. A better understanding of the conditions and components involved in these complex systems is needed to assess the mobility, release and availability of Cu.

5. Future research plan

Additional research is needed to understand specific ferrihydrite characteristics and how these are modified by organic matter. Measurements of BET surface area, surface charge (PZC), electrophoretic mobility and particle/aggregate size, X-ray diffraction for mineral phase confirmation are needed to be able to assess and model these interactions more properly. In the case of organic matter, it is important to determine the speciation of the carbon source, which surface groups are present and more prevalent and CHNS analysis for differences in coprecipitated organic matter. Further high resolution TEM imaging and kinetic experiments will be needed to determine any differences between sorption and coprecipitation products.

Future experiments will also focus on distinguishing the form of Cu in the solid phase, i.e. within the oxide structure, sorbed to the surface, or chelated by OM. Also, an asymmetric flow field flow (AF4) coupled to an online TOC analyzer will be needed to determine aggregate size and carbon and metal content per size fraction. This will allow distinguishing between labile, dissolved and truly dissolved extractable Cu concentrations to be able to determine bioavailability. The ultimate objective would be to apply Cu availability knowledge to other processes present in these complex geochemical systems, such as denitrification, and understand how they are affected.

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