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

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HIGHLIGHTS

- Sorption or coprecipitation products of copper, iron and humic acids are compared.
- At low humic acid concentration, coprecipitation products enhanced Cu sorption.
- Cu sorption and coprecipitation increased with increasing humic acid below pH 5.5.
- Cu extraction was typically higher from coprecipitation products.

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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 organo-mineral 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.

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

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

2.1. Reagent preparation

Stock solutions of $NaNO_3$, $Cu(NO_3)_2$, $Fe(NO_3)_3$, and $Ca(NO_3)_2$ 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 MΩ deionized water (DI) and containers were acid washed in 10% HNO_3 for 24 h 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 $NaNO_3$, 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 min. 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 μm 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 $NaNO_3$ 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 μg in each experimental extraction in order to compare readily between precipitation materials. For the extractions, the slurry solution was mixed with either Ca^{2+}, L-glycine, L-histidine, or citric acid at a Cu:extractant molar ratio of 1:20 with a background 10 mM $NaNO_3$ solution at pH 6. For pH desorption reactions, a background 10 mM $NaNO_3$ solution pre-adjusted to pH 4−6 was added to the slurry. Triplicates vials were rotated for 24 h prior to filtration and analysis.