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Structural stability of coprecipitated natural organic matter and ferric iron under reducing conditions

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a b s t r a c t

The objective was to assess the interaction of Fe coprecipitated with dissolved organic matter (DOM) and its effect on Fe (hydr)oxide crystallinity and DOM retention under abiotic reducing conditions. A Fe-based coagulant was reacted with DOM from an agricultural drain and the resulting precipitate (floc) was exposed to S(II) and Fe(II). Solution concentrations of Fe(II/III) and DOM were monitored, floc crystallinity was determined using X-ray diffraction, and the composition and distribution of functional groups were assessed using scanning transmission X-ray microscopy (STXM) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. Results indicate coprecipitation of Fe(III) with DOM forms a non-crystalline floc that withstands crystallization regardless of change in pH, Fe:DOM ratio and type of reductant added. There was no evidence that exposure to reducing conditions led to release of DOM from the floc, indicating that coprecipitation with complex natural DOM in aquatic environments may stabilize Fe (hydr)oxides against crystallization upon reaction with reduced species and lead to long term sequestration of the DOM. STXM analysis identified spatially distinct regions with remarkable functional group purity, contrary to the model of DOM as a relatively uniform complex polymer lacking identifiable organic compounds. Polysaccharide-like OM was strongly and directly correlated with the presence of Fe but showed different Fe binding strength depending on the presence of carboxylic acid functional groups, whereas amide and aromatic functional groups were inversely correlated with Fe content.

1. Introduction

The coprecipitation of Fe and dissolved organic matter (DOM) is common in soil, sediments, surface water and subsurface aquifers, systems that experience significant variation in either redox or pH conditions (Fuller et al., 1993; Pokrovsky and Schott, 2002). These interactions are hypothesized to play a role in immobilizing DOM and stabilizing it against microbial degradation, as well as controlling the structure and reactivity of natural Fe (hydr)oxides (von Luetzow et al., 2006; Eusterhues et al., 2008). Thus, OM–Fe coprecipitates represent an important class of structures whose chemistry and reactivity require further understanding under different environmental conditions since Fe speciation and mobility affect the availability, cycling, and transport of metals, OM and nutrients.

Coprecipitation of Fe and DOM can occur where reduced water (e.g. lake sediments, mine drainage water, aquifers) comes into contact with oxidized water, causing soluble Fe(II) to be transformed to relatively insoluble Fe(III), which concurrently surcos ions and compounds such as metals and OM (Fuller et al., 1993). In estuarine environments, coprecipitation of OM and Fe oxides occurs where salinity causes an increase in the ionic strength of incoming freshwater and subsequent precipitation (Sholkovitz, 1976). Similar phenomena occur in saturated soil exposed to air, such as in wetlands.

In a process that mimics natural coprecipitation of Fe and DOM, the water treatment industry frequently uses Fe-based salts to remove DOM from water prior to disinfection (Dempsey et al., 1984; Siéliéchi et al., 2008). The technique is used to prevent formation of carcinogenic halogenated byproducts (e.g. chloroform) during disinfection, which result from reaction of chlorine with DOM. The resulting precipitate is an organo-Fe complex, commonly termed “floc.” While the floc resulting from coagulation in water treatment is typically disposed of in landfills, there are cases where reservoirs or constructed wetlands are used as settling ponds to retain the residual floc (Bachand et al., 2000, 2006; Downing et al., 2008). The use of on-site coagulation to remove DOM and improve agricultural drainage water quality is underway in the Sacramento-San Joaquin Delta (Mourad, 2003; Henneberry et al., 2011). Accumulation of the resulting floc in constructed wetlands is intended to help reverse land subsidence in the region. One of the main
uncertainties regarding both natural and synthetic Fe–DOM complex effects their stability under changing environmental conditions. For example, if small changes in pH or redox conditions cause significant re-release of DOM, then the ability of the method to immobilize and stabilize DOM over the long term would be greatly diminished.

Studies of DOM Fe (hydr)oxide structures have found greater structural disorder in the coprecipitated Fe phases vs. organic-free or synthetic ferrithydrate (Eusterhues et al., 2008; Mikutta et al., 2008; Cismasu et al., 2011; Mikutta, 2011). The implications of these structural changes on biogeochemical processes remain unresolved. Under low DOM or DOM-free conditions, poorly crystalline Fe (hydr)oxides like ferrithydrate are highly reactive and a dominant adsorbent of metals and nutrients in aquatic and terrestrial systems, even at low Fe concentration (Larsen and Postma, 2001; Hiemstra and Van Riemsdijk, 2009). However, these poorly crystallized minerals have also been found to be highly susceptible to microbial reduction and dissolution in both soil and aquatic environments (Glaser et al., 2003; Weiss et al., 2004). They may thus recrystallize into more ordered, lower surface area Fe minerals, such as goethite or magnetite, with subsequent decrease in reductive potential and sorptive capacity.

The presence of various ions and electron donors in solution has been found to both catalyze and inhibit the crystallization of ferrithydrate (Wehrl et al., 1989). Fe(II), formed either abiotically or via Fe reducing microorganisms, has been found to catalyze the transformation of ferrithydrate into more crystalline materials such as goethite and magnetite (Benner et al., 2002; Tufano et al., 2009). However, only a few studies have investigated the effect of OM on the reactivity of poorly crystalline ferric (hydr)oxides under reducing conditions. In these studies, OM has been found to both enhance and inhibit crystallization of ferrithydrate under aerobic and anaerobic conditions (Cornell and Schwertmann, 1979; Cornell and Schneider, 1989; O’Loughlin et al., 2010). Most of the studies used simple or synthetized organic compounds such as citric and tartaric acids and oxalate rather than more complex, naturally occurring OM. As DOM is composed of a diverse array of components, there is a need to determine the effect that coprecipitation with natural, structurally heterogeneous OM has on Fe reactivity. In addition, studies that focus on the effect of multiple reducing agents on Fe-mineral reduction are lacking. Such knowledge is important in order to predict the fate of poorly crystalline iron (hydr)oxides in environments such as wetlands that experience fluctuating pH and redox conditions.

The two primary objectives of this study were to (i) determine the impact of DOM on the propensity of poorly crystalline Fe (hydr)oxide to recrystallize into more stable lower surface area phases and (ii) determine floc stability, defined as the ability to retain OM under reducing conditions. Reducing conditions were simulated by addition of Fe(II) or S(-II). Scanning transmission X-ray microscopy (STXM) was used to examine Fe–OM interactions, and X-ray diffraction (XRD) to monitor changes in floc crystallinity, and solution characteristics to assess DOM and Fe release over time.

2. Materials and methods

2.1. Incubation experiments

Water samples were collected on September 15, 2010 from an agricultural drain on Twitchell Island receiving rice field effluent. Twitchell Island is on the western portion of the San Francisco Bay Delta (California, USA). In the late 1800s the island, formerly a wetland, was drained for agricultural purposes. Current land use on the island includes rice farming, livestock pasture, corn, alfalfa and constructed wetlands. Dissolved organic carbon (DOC) concentration in the drainage water typically ranges between 0.5 and 7.5 mmol l\(^{-1}\) (Deverel et al., 2007; Kraus et al., 2008). Soil on the island is Rindge mucky silt loam (Eucic, thermic Typic Haplorgapturb), formed from Tule and reed deposition (Tugel, 1993).

A sample of agricultural drainage water was collected using an Amazon submersible pump and high purity, plasticizer-free 1.27 cm Tygon tubing. The water was filtered directly in the field through a 0.2 μm in-line membrane filter (General Electric Membrane, 25.4 cm). Samples were directly transferred to a clean 191 Al ball lock soda keg. Water was stored in the dark at 4°C for ca. 2 weeks prior to experimental procedures and analysis.

As the water may have reached anoxic conditions due to the combination of high daytime temperature and stagnant water conditions within the drain, the sample was purged with O\(_2\) (2 h) prior to experimentation to ensure that DOM and Fe concentration would resemble that of aerated flowing water typically found in the drains. After oxidation, water was passed through 0.3 μm ashed, quartz fiber filters.

A coagulant solution (1.75 M) was made by mixing Fe\(_2\)(SO\(_4\))\(_3\) powder in reagent grade 9 M H\(_2\)SO\(_4\). The amount of coagulant required to remove the maximum amount of DOC was determined using a streaming current detector (SCD), a common method used by water utilities to determine coagulant dosing requirements. The SCD measures the electrical charge on colloids in water and is an indicator of the extent of destabilization (Dentel and Kingerly, 1989). Optimal dose is reached when the SCD indicates a neutral indicator. The amount of C and Fe in the floc was calculated as the difference between the concentration in solution prior to and following coagulation (after filtration through a 0.2 μm membrane). The ratio of DOC in solution to Fe added as coagulant was varied, resulting in 47–78% DOC removal and floc molar C:Fe values from 1.9 to 3.5, representing maximum DOC removal conditions to lesser values, respectively (Table 1).

Coagulation of solutions varying in initial C:Fe values was conducted using a six paddle mixer (Phipps and Bird 900, Richmond, VA, USA) at 250 rpm for 3 min and 40 rpm for 15 min. Final pH was adjusted to 6.5 ± 0.1 with 5 M NaOH. The solutions were left (1 h) to allow flocculation to be complete. Aliquots (50 ml) were transferred from the batch solutions, with stirring (magnetic bar), to 50 ml crimp-top glass serum vials with rubber butyl septa and Al rings.

In an unbuffered system, the addition of Fe(II) and S(-II) results in a decrease and increase in pH, respectively. To remove the effect of pH, which could potentially confound stabilization (Schwertmann and Murad, 1983), we added PIPES (1,4-piperazinediethane sulfonic acid) buffer to maintain a system at 6.5 pH. The PIPES buffer was chosen because it does not react with Fe species; however, it is a concentrated organic compound and thus masks change in DOC concentration in the system. We therefore conducted two experiments: (i) an unbuffered system, in which floc C:Fe ranged from 1.9–2.4 and (ii) a buffered system with floc C:Fe between 2.5 and 3.5 (Table 1). In the unbuffered system, the samples were pipetted as above into serum vials. In the buffered system, PIPES was added after the addition of NaOH, to a final concentration of 7 mM.

All sample preparation and extractions were conducted in an anaerobic glove box maintained under a N\(_2\) atmosphere (specialty grade, 99.9%). Samples were sparged with N\(_2\) (15 min) before being transferred to the anaerobic chamber.

The effect of two different reductants, Fe(II) and sulfide S(-II), on floc crystallinity was tested. Fe(II) was added by injecting a concentrated stock solution (0.001 M or 0.1 M) of FeSO\(_4\) to a final concentration between 0.01 mM and 3.97 mM (Table 1). S(-II) was added via injection of a stock solution of Na\(_2\)S (0.01 M or 0.1 M) to a solution concentration range of 0.05–0.6 mM. Concentration values of the
Fe(II) were selected to mimic those in natural wetlands (below detection to 300 μM; Blodau et al., 2002; Emerson and Weiss, 2004; Knorr et al., 2009) to values resulting in an Fe(III):Fe(II) of 1–1.8. S(-II) concentrations were selected to cover the range of values for wetlands (0–6.2 mM; Blodau et al., 2002; Choi et al., 2006).

To determine whether the presence of DOM affected floc re-crystallization, all reducing treatments were also applied to vials containing coagulant added to DI water with no DOM. To ensure crystallization of Fe did not occur in the absence of reductant, samples (both with and without OM), that did not receive reductant, were also examined.

Treatments were conducted in triplicate except for the buffered treatment with a higher ratio of C:Fe (3.5; Table 1), which was not replicated. All samples were destructively sampled on days 0 (2–3 h following initial preparation), 5 and 14.

2.2. Solution analysis

DOC concentration was determined by UV-persulfate digestion (Teledyne-Tekmar Phoenix 8000). The absorption at 254 nm was measured on filtered samples at constant temperature (25 °C) with a Cary 300 spectrophotometer using a 1 cm quartz cell and distilled water as blank. To eliminate interference from Fe(III) in absorbance (UV) measurements, 0.05 ml 5% hydroxylamine hydrochloride was added to 1 ml sample and absorbance data recorded until no further change, indicating that all the Fe(III) had been reduced to non-interfering Fe(II), a process that takes ca. 10 min (Doane and Horwath, 2010). Specific UV absorbance (SUVA), a proxy for aromaticity, was calculated by dividing absorbance at 254 nm by DOC concentration, and is reported in 1 mg C m−1 m−1 (Weishaar et al., 2003). Total dissolved Fe, Fe(II) and Fe(III) were determined colorimetrically with ferrozine (Viollier et al., 2000; Pullin and Cabaniss, 2001). One way ANOVA was used to determine significant differences between DOC concentration and SUVA values using the R statistical program (version 2.10.1). Initial water quality characteristics can be found in Table 2.

2.3. Floc analysis

2.3.1. STXM

The detailed C and Fe associations in fresh aerated sample floc material were investigated using STXM in conjunction with near edge X-ray fine structure (NEXAFS) spectroscopy at beamline 5.3.2.2 of the Advanced Light Source Facility in Berkeley, California (Warwick et al., 2002). Samples were prepared by pipetting small aliquots of freshly prepared floc onto a 100 nm thick Si3N4 membrane, followed by transfer to the sample chamber maintained under a He atmosphere. Carbon NEXAFS spectra were collected from 280 eV to 330 eV and Fe spectra from 700 to 730 eV. Functional

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Initial treatment solution conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Treatment</strong></td>
<td><strong>Fe(III) added as coagulant (mmol l−1)</strong></td>
</tr>
<tr>
<td>Unbuffered treatments</td>
<td></td>
</tr>
<tr>
<td>Unbuffered, higher concentration of coagulant added</td>
<td>3.7</td>
</tr>
<tr>
<td>Unbuffered, lower concentration of coagulant added</td>
<td>2.2</td>
</tr>
<tr>
<td>Buffered treatments</td>
<td></td>
</tr>
<tr>
<td>Buffered, higher concentration of coagulant added</td>
<td>2.2</td>
</tr>
<tr>
<td>Buffered, lower concentration of coagulant added</td>
<td>1.3</td>
</tr>
</tbody>
</table>

* Ratio of initial floc prior to reductant addition.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Initial water quality characteristics of rice drain water.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DOC (mmol l−1)</strong></td>
<td><strong>pH</strong></td>
</tr>
<tr>
<td>0.9</td>
<td>8.4</td>
</tr>
</tbody>
</table>

* Electrical conductivity.  
** Total dissolved iron.

3. Results and discussion

3.1. STXM characterization of fresh floc material

The use of STXM provides spatially resolved elemental and chemical information for a sample not under high vacuum conditions, making it an ideal tool for floc analysis. The distributions of C and Fe in three separate flocs were identified; two are shown in Fig. 1. In general, C was highly spatially correlated with Fe in both floc particles, with the exception of Regions 1 and 2, which show no detectable Fe concentration (Fig. 1a). Fig. 1c shows the relative distribution of OM functional groups for the particle depicted in Fig. 1a, with aromatic rich OM in red (285.5 eV), amide rich OM in...
blue (288.3 eV) and carboxylic rich OM in green (288.7 eV). The functional group distribution for the particle in Fig. 2b was more uniform and the image shown represents the intensity at O-alkyl material (289.5 eV) (Christl and Kretzschmar, 2007; Chan et al., 2009). Interestingly, in Fig. 1a the OM associated with the Fe material is carboxyl rich, while both the amide and aromatic rich areas are inversely correlated with Fe content (Fig. 1a and c).

Corresponding NEXAFS spectra for the floc particles were also collected for C and Fe. The shape of the spectra is sensitive to the composition of the corresponding material. The C spectrum associated with Region 1 (Fig. 1d) shows a large peak at 285.5 eV assigned as aromatic C, while the Region 2 spectrum has, as the major feature, a peak at 288.3 eV associated with amide functionality (Cismasu et al., 2011). The Region 3 spectrum, which comprises the bulk of the floc, as well as the spectrum from a third floc particle (not shown), is dominated by the 288.7 eV feature, indicating a large fraction of carboxyl groups, and a shoulder at ca. 287.5 eV associated with polyvalent metal complexation of carboxyl groups (Armbruster et al., 2009). The Region 4 spectrum is dominated by a 289.5 eV feature associated with O-alkyl material and consistent with non-carboxyl containing polysaccharides (Christl and Kretzschmar, 2007; Chan et al., 2009). Comparison of the Fe NEXAFS spectra from Regions 3 and 4 shows a distinct shoulder at 708.5 in Region 3 spectra, largely absent from the Region 4 spectra (Fig. 1e). In addition, the position of the dominant peak shifts to slightly lower energy from Region 3 to Region 4, 710.3 to 709.9 respectively. Another particle, not shown, exhibits similar C and Fe NEXAFS spectra to that of Region 3. The primary inference to be made from the differences in the Fe NEXAFS is that Fe spectral shape appears to correlate with the functional group characteristics of the associated C. This implies that the majority of Fe atoms in the floc are directly associated with C functional groups, in contrast to a conceptual model in which the OM is only associated with the surface of a Fe mineral phase. The specific shape of the Fe NEXAFS spectra is determined by three factors: electrostatic multiplet effects, ligand field effects and degree of bonding covalency (Hocking et al., 2010). The less distinct shoulder at 708.5 eV in the Region 3 spectra implies that the Fe–OM complexes in this floc have either lower crystal field stabilization or greater orbital covalency.

The highly distinct nature of the individual C NEXAFS spectra (Fig. 1d) contrasts with the remarkable similarity of C NEXAFS spectra of bulk DOM reported by Schumacher et al. (2006) and Christl and Kretzschmar (2007). This emphasizes that, while bulk
analysis of DOM can provide information regarding average molecular properties, DOM most likely consists of multiple chemical domains, each largely homogenous and distinct. Moreover, it is interesting that the process of precipitation and complexation with Fe alone appears sufficient to physically and chemically separate these domains. This implies that these chemically distinct groups are relatively loosely associated with each other.

The propensity of polysaccharide C to associate with Fe is supportive of the bulk fractionation observed by Eusterhues et al. (2011). The varying electronic environment of the Fe atoms with the binding strength of the DOM implies that isolated or very small clusters of Fe centers are in direct molecular association with the carboxyl or hydroxyl functional groups. It has been observed that the size of the crystalline regions of precipitated Fe hydroxide material can be diminished in the presence of OM (Cismasu et al., 2011) and our results appear to represent an extreme case of this phenomenon, possibly due to higher C:Fe values.

3.2. Flocc reactivity

3.2.1. DOC concentration and SUVA characteristics vs. time

Although pH was adjusted initially to 6.5, upon addition of Fe(II) the pH of the unbuffered treatments dropped to 4.6–5.4. In con-

Table 3
Iron concentration and pH upon addition of reductants (Y, yes; N, no; s.d., standard deviation; n.d., no detection; data for samples with no DOM can be found in the Supplementary Table).
3.2.2. Effect of Fe concentration

Total Fe concentration in the low Fe(II) treatments (0.01 mM) was below raw water solution concentration for the unbuffered treatments (Table 3) and below detection (0.36 mM) for all unbuffered treatments containing no DOM, except for the day 0 treatments receiving a coagulant addition of 2.2 mmol l\(^{-1}\) Fe (Supplementary information). For both the buffered and unbuffered treatments receiving equimolar addition of Fe(II) and Fe(III) in the coagulant [2.3–3.8 mM Fe(II)], some Fe(II) – up to 20% – was initially lost from solution on day 0. There was a general increase in total solution Fe on day 5 followed by a decrease on day 14 (Table 3). Fe(III) release from both buffered and unbuffered treatments coprecipitated with DOM was close to zero (Table 3).

The decrease in solution Fe(II) in the treatments receiving equimolar Fe(II) is most likely due to the association of the reductant with the surface of Fe (hydr)oxide centers within the floc or unsatisfied complexation sites within the OM. The release of Fe(II) towards the middle of the incubation, especially for samples with no OM, most (Pedersen et al., 2005) likely resulted from the reductive dissolution of floc by added Fe(II) (Wehrli et al., 1989). Fe(II)-catalyzed dissolution of Fe(III) has been found to occur but it is interesting to note that the release of Fe(III) in treatments lacking DOM was higher than those coprecipitated with DOM (Supplementary table), as this indicates DOM may reduce the reactivity of the Fe (hydr)oxide. As discussed in Section 3.1, carboxylic acids play a large role in the complexation during coprecipitation and coagulation. This strong, inner-sphere complexation of carboxylic groups with the Fe (hydr)oxide group may have interfered with the Fe(II) mediated dissolution of Fe(III).

3.2.3. Effect of sulfide concentration

In treatments that received a lower S(-II) concentration (0.05 mM), small amounts of Fe(II) were present in solution immediately after S(-II) addition, but gradually decreased to or below detection limit in most treatments (Table 3). Little to no dissolution of Fe(II) (<0.4% of floc) occurred with addition of higher S(-II) (0.6 mM) in spite of visual darkening indicative of FeS formation. Previous studies that used ferrihydrite and poorly crystalline iron oxides to remove sulfide from water have also found release of dissolved Fe to be negligible (Poulton, 2003).

S(-II) is known to react with Fe oxide species through an inner-sphere complexation and subsequent electron transfer to the Fe(III) species (Afonso and Stumm, 1992), so the initial release of Fe for the lower S(-II) treatments is most likely due to reductive dissolution of the floc surface by the added S(-II). The Fe(II) released initially may have reacted with unreduced floc Fe or with the additional S(-II) in solution to form a secondary solid Fe(II)-sulfide species (Poulton, 2003; Slowey and Brown, 2007).

A higher concentration of S(-II) has been found to result in enhanced rates of Fe-sulfide precipitate formation (Pyzik and Sommer, 1981), which may be why Fe release was lower for this treatment than treatments with a lower concentration of S(-II). However, no iron sulfide minerals were detected via XRD analysis (Section 3.3) although this could be due to the limited sensitivity of XRD to small grain size or short-range order material. In spite of these obvious changes in Fe chemistry there was, however, no significant release of DOM to solution.

3.3. Floc crystallinity

X-ray diffraction was used to determine the formation of more crystalline Fe oxides and sulfides. There was no apparent development of crystallinity nor even formation of ferrihydrite-like characteristics in treatments that did not receive Fe(II) or S(-II) over the 14 day incubation period (see Fig. in Supplementary information). This implies that the presence of an electron donor was required for crystallization of Fe(III) under experimental conditions. All DOM-free treatments that received either Fe(II) or S(-II) formed goethite peaks by day 5 and an unidentifiable peak for the treatment receiving the lower dose of S(-II) (Figs. 4 and 5). In contrast, there was no apparent crystallization for samples containing Fe...
coprecipitated with DOM, even by day 14 for both unbuffered and buffered treatments. This indicates that coprecipitated OM inhibited reductive crystallization of the Fe (hydr)oxides during the 14 day period. As there was no obvious difference in crystallization character between the unbuffered and buffered XRD spectra, the Figs. and the discussion below reflect data from the buffered treatments.

Higher addition of Fe(II) in the DOM-free treatments resulted in formation of mainly goethite peaks by day 5 (Fig. 4). Although goethite is a common species formed upon reductive transformation of poorly crystalline Fe (hydr)oxides (Cornell and Schneider, 1989; Kukkadapu et al., 2003), the lack of magnetite formation is in contrast to previous findings (Hansel et al., 2005; Yang et al., 2010). The formation of minerals on day 5 coincides with the increase in soluble Fe(II) in solution, supporting re-crystallization to lower surface area mineral phases with lower Fe(II) adsorption capacity (Wehrli et al., 1989).

Treatments with no DOM that received the lower S(II) amendment showed increased crystallinity by day 5, with more
prominent goethite peaks (Fig. 5) vs. both the high Fe(II) and high S(II) treatments. On the other hand, treatment in the absence of DOM amended with the higher concentration of S(II) crystallized immediately, forming goethite, and eventually akageneite (Fig. 5).

As S(II) is a stronger reductant for Fe(III) than Fe(II), the rate of electron exchange and subsequent formation of secondary minerals is most likely higher for S(II), resulting in an enhanced rate of mineral formation than for the Fe(II) treatments. The higher S(II) treatments may have immediately formed poorly crystalline iron-sulfide complexes with the floe, as indicated by the darkening of the samples upon S(II) addition. The formation of iron sulfide species may have competed with other mineral formation, resulting in less prominent peaks than those for the low S(II) addition. While no FeS minerals were identified in the XRD analysis, this does not preclude the presence of small particle size, poorly ordered FeS, such as Fe monosulfide, common in wetland soils of the region (Maynard et al., 2011). In the low S(II) treatments, there may have been more available Fe(II) in solution due to the lower concentration of S(II), which is important for the amount and species of secondary minerals formed (Tufano et al., 2009).

4. Summary and implications

The presence of coprecipitated OM strongly inhibited the reductive crystallization of Fe (hydr)oxide materials. The DOM–Fe (hydr)oxide interaction produced a stable floe material that did not release DOM back into solution regardless of pH, Fe:DOM ratio and type of reductant added. The results indicate the potential usefulness of Fe–DOM complexation in the long term removal of DOM from wetland environments as well as the importance of Fe–DOM complexes for OM stabilization in soil, even under reducing conditions. In addition, they illustrate that, although coprecipitated Fe phases decreased structural order, they may not in fact be more reactive.

The mechanism of coagulation and coprecipitation may result in different bond strength and molecular conformations from adsorption of OM to pre-formed Fe (hydr)oxides. Coprecipitation may result in reconfirmation of the OM around the positively charged Fe, resulting in micellar interactions and tighter coiling of DOM (Jung et al., 2005; Siélièchi et al., 2008). This reconfirmation, in addition to the strong inner sphere complexation of carboxylic acids – evidence by quantum chemical calculations. Journal of Electron Spectroscopy and Related Phenomena 169, 51–56.


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