



Dissolved organic carbon retention by coprecipitation during the oxidation of ferrous iron



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ABSTRACT

The adsorption of dissolved organic carbon (DOC) on iron (Fe) (hydr)oxides represents an important stabilization mechanism for soil organic matter (OM) and contributes to soil C accumulation. However, in soils that experience periodic fluctuations in redox conditions the interaction between DOC and Fe (hydr)oxides may not only involve organic coatings on mineral surfaces, but also Fe-DOC coprecipitates that form during the oxidation of soil solutions containing important amounts of DOC and Fe²⁺. The aim of this work is to provide new insights into the mechanisms involved, and the amount and selectivity of C retained during the coprecipitation process. A series of Fe-OM associations with increasing C loading was synthesized at pH 6 by surface adsorption or coprecipitation (oxidation of ferrous iron) utilizing rice-straw derived dissolved organic matter. The kinetics of Fe²⁺ oxidation and complexation, and the total and selective retention of DOC during the coprecipitation process were evaluated. Moreover, synthesized associations, as well as a field coprecipitate collected in situ from a paddy soil, were studied by X-ray diffraction, N₂ gas adsorption-desorption isotherms, electrophoretic mobility measurements and thermogravimetric analyses. Coprecipitation resulted in higher organic C contents (49–213 mg g⁻¹) with respect to adsorbed systems (18–47 mg g⁻¹), and favoured the inclusion of OM within highly aggregated associations having particularly low BET specific surface areas. Although coprecipitation led to a strong, selective retention of aromatic constituents, the initial complexation of Fe²⁺ by aliphatic carboxylic moieties and precipitation as C-rich Fe-OM associations contributed to the total C retention, particularly at higher solution C/Fe ratios. These aliphatic complexes formed during coprecipitation may play an important, though often underestimated, role in C stabilization in soils experiencing frequent redox fluctuations and often characterized by elevated soluble Fe²⁺ and DOC concentrations.

1. Introduction

Sorption of dissolved organic matter (DOM) onto iron (Fe) (hydr)oxides is known to play an important role in the stabilization and accumulation of organic carbon (C) in soils (Eusterhues et al., 2005; Kaiser and Guggenberger, 2000). However, in hydromorphic soils the retention of organic C by soil minerals and its subsequent stabilization against microbial decomposition largely depends on redox state (Kögel-Knabner et al., 2010). In fact, changes in soil redox conditions can strongly influence the association between Fe (hydr)oxides and soil organic matter (OM) with important implications on C stabilization.

Paddy soils are hydromorphic soils formed under intense anthropogenic influence and generally subjected to periodically fluctuating redox conditions induced by specific agricultural management practices

(flooding, puddling and drainage; Kögel-Knabner et al., 2010). These soils are known to accumulate significant amounts of OM in the topsoil (Wissing et al., 2014), however the mechanisms of OM accumulation under paddy management are not well understood. Apart from the incomplete decomposition of OM under anaerobic conditions (i.e. biological capacity; see Baldock et al., 2004), direct interactions with ubiquitous Fe (hydr)oxides (i.e. chemical protection) may contribute significantly to the long-term stabilization of OM (Wissing et al., 2013).

Reductive dissolution of Fe (hydr)oxides under anoxic conditions releases Fe²⁺ into solution which may be readily oxidized by O₂ and precipitated in the form of short-range ordered hydroxides such as ferrihydrite, when oxic conditions are rapidly re-established (Said-Pullicino et al., 2016; Schwertmann, 1991). Under these conditions, highly disordered Fe phases often form in the presence of elevated

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concentrations of DOM through the process of coprecipitation. In contrast to surface adsorption, coprecipitation may involve different mechanisms of Fe-OM association, namely inclusion (i.e., included within the crystal structure) and occlusion (i.e., physical entrapment within the growing crystal), as well as adsorption on neoformed (hydr)oxides (Kleber et al., 2015 and references therein). Unlike adsorption, where DOM is mainly retained by ligand exchange at the surface of pre-existing Fe oxides, coprecipitation may result in the formation of a mixture of pure and OM-rich Fe (hydr)oxides, and precipitated insoluble Fe-OM complexes (Chen et al., 2014; Kleber et al., 2015). The high concentrations of DOC that often accumulate in paddy topsoils under anoxic conditions (Said-Pullicino et al., 2016) may favour the formation of aqueous organic Fe²⁺ complexes (Henneberry et al., 2012; Jones et al., 2015) that may precipitate and contribute to C retention during the formation of Fe-OM coprecipitates under subsequent oxic conditions.

Coprecipitation may result in different mineral surface properties (e.g. specific surface area, surface charge, particle aggregation/dispersion) with respect to adsorption (Mikutta et al., 2014), and may consequently affect the reactivity and stability of these Fe-OM associations (Chen et al., 2014; Eusterhues et al., 2014). Recently, various studies have evaluated the mechanisms of formation, properties and reactivity of Fe-OM phases derived from coprecipitation with different OM sources, such as forest-floor DOM (Chen et al., 2014; Eusterhues et al., 2008, 2011; Mikutta et al., 2014), lignin and hydroxybenzoic acids (Eusterhues et al., 2011; Mikutta, 2011), humic and fulvic acids (Angelico et al., 2014; Pédrot et al., 2011; Shimizu et al., 2013), and polysaccharides (Mikutta et al., 2008). Depending on the DOM composition contrasting results have been reported as to whether coprecipitation actually leads to a greater C retention with respect to adsorption. Nonetheless, these works generally agree that the mechanisms involved, and the amount and selectivity of C retained during coprecipitation is highly dependent on the composition of the solution from which they precipitate. Most studies considered the coprecipitation of DOM during the hydrolysis of Fe³⁺, but only a few studies have evaluate the coprecipitation process during the oxidation and hydrolysis of Fe²⁺ at circum-neutral pH, which is generally considered as the main process responsible for the formation of coprecipitates in soils subjected to alternating redox conditions. Moreover, few studies have evaluated this process in paddy soils where rice straw decomposition is the main contributor to the DOM pool.

Based on these considerations we hypothesized that during the oxidation and hydrolysis of Fe²⁺ in the presence of straw-derived DOM, (i) coprecipitation may lead to a greater retention of organic C with respect to surface adsorption; (ii) increasing amounts of DOC with respect to Fe (increasing initial C/Fe ratio) may favour the contribution of Fe-OM complexation and precipitation to the total C retained by coprecipitation, and also hinder the homogeneous nucleation of Fe (hydr)oxide nuclei, thus affecting the size and structure of the Fe (hydr)oxide formed; and (iii) the selective retention of particular organic constituents depends on the relative contribution of Fe-OM complexation and adsorption processes during coprecipitation. We tested these hypotheses by synthesizing a series of Fe-OM associations with increasing C/Fe ratios at pH = 6 prepared by either surface adsorption (SA) or coprecipitation (CP) of rice straw-derived DOM. In order to gain insights into the coprecipitation process we evaluated the kinetics of Fe²⁺ oxidation and complexation, and the total and selective retention of DOC. The synthesized associations were then characterized by physicochemical, spectroscopic and thermal analyses. A natural Fe-OM coprecipitate was also obtained by in situ sampling of paddy soil solutions from the anaerobic topsoil during a cropping season and subsequent oxidation in order to compare the obtained material with laboratory-synthesized coprecipitates.

Table 1

Chemical characteristics of the rice straw-derived DOM used in this study.

Parameter	Value
C (mg g ⁻¹) ^a	304
N (mg g ⁻¹) ^a	111
H (mg g ⁻¹) ^b	391
O (mg g ⁻¹)	258
C/N	27.3
COOH acidity (mmol mol ⁻¹ C) ^b	23.2
Phenolic acidity (mmol mol ⁻¹ C) ^b	49.7
C distribution (%) ^c	
Alkyl C	22.6
Methoxy/amine C	8.3
O-Alkyl C	37
Aromatic C	19.8
Carboxyl C	6.7
Carbonyl C	5.6
Anions ^d (mmol g ⁻¹ C)	
Cl ⁻	24.1
NO ₃ ⁻	nd
SO ₄ ²⁻	0.1
HPO ₄ ⁻	1.2
H ₄ SiO ₄	1.7
Cations ^e (mmol g ⁻¹ C)	
K ⁺	19.6
Ca ²⁺	4.9
Fe ³⁺	0.03

^a Determined by dry combustion.^b Total and carboxyl acidity were determined by potentiometric titration with Ba(OH)₂ and Ca-acetate, respectively.^c Determined by ¹³C NMR spectroscopy.^d Determined by ion chromatography, except for Si that was determined spectrophotometrically.^e Determined by atomic absorption spectroscopy.

2. Materials and methods

2.1. Rice straw-derived dissolved organic matter extraction

Rice straw (cut into 1–2 cm segments) was soaked in deionized water (straw-solution ratio of 1:30), inoculated with a paddy soil extract (Haplic Gleysol, NW Italy) and incubated for 30 days at 25 °C under oxic conditions to simulate field conditions after crop residue incorporation. Redox potential (Eh) and dissolved O₂ concentrations, determined potentiometrically and polarographically respectively, were monitored regularly and adjusted by bubbling air through the suspension to ensure oxic conditions. A preliminary test showed that under these conditions straw extracts with a relatively high DOC concentration (≈ 450 mg C l⁻¹) and a significant proportion of aromatic constituents (specific UV absorption at 254 nm ≈ 1.8 l mg⁻¹ m⁻¹) could be obtained. The suspension was filtered through 0.45 μm cellulose acetate filters and freeze-dried. Table 1 presents the chemical characteristics of the rice straw-derived DOM used in this study.

2.2. Synthesis of ferrihydrite and Fe-OM associations

Ferrihydrite (Fh) was prepared by rapidly oxidizing 2 l of a solution of 2 mM FeCl₂ at pH 6 in a stirred vessel by bubbling O₂ at a rate of 200 ml min⁻¹ until complete oxidation evaluated through the disappearance of Fe²⁺ from solution. Considering the important influence of Si on the structure of ferrihydrite (Karim, 1984; Schwertmann and Thalmann, 1976), silicic acid was added before oxidation to obtain a Si concentration of 0.4 mM and an initial molar Si/Fe ratio of 0.2. This amount was equivalent to the maximum amount of Si present in the rice straw-derived DOM solutions used in this work. At this Si/Fe molar ratio the formation of green rust is inhibited and ferrihydrite is the ultimate oxidation product (Karim, 1986). During oxidation the pH was maintained at 6.0 by progressive addition of 0.25 M KOH by means of an automatic titrator (TTT85 titrator and ABU80 autoburette,

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