

INFLUENCE OF ADSORPTION vs COPRECIPITATION ON THE RETENTION OF RICE STRAW-DERIVED DISSOLVED ORGANIC CARBON AND SUBSEQUENT REDUCIBILITY OF Fe-DOC SYSTEMS Marcella SODANO Cristina LERDA Maria MARTIN Luisella CELI Daniel SAID-PULLICINO Soil Biogeochemistry Team Rice Agro-ecosystem & Environmental Research DiSAFA – University of Torino, Italy



Rationale

The dissimilatory reduction of Fe oxides is the main organic C-consuming process in paddy soils under anoxic conditions. This biotic process depends on the availability of labile organic matter (e⁻ donors) and a reducible Fe pool (e⁻ acceptors). Apart from contributing to C stabilization, the interaction between Fe oxides and dissolved organic C (DOC) may influence the structure and reactivity of these natural oxides, and selectively influence the chemical properties of DOC. In soils that are regularly subjected to fluctuations in redox conditions DOC retention by Fe oxides may not only involve organic coatings on mineral surfaces, but also Fe-DOC coprecipitates that form during the rapid oxidation of soil solutions containing important amounts of DOC and Fe(II).

Hypotheses

We hypothesized that coprecipitation may retain greater amounts of DOC with a greater affinity for the more aromatic constituents with respect to adsorption.





CP resulted in a higher retention of DOC with respect to SA. Whereas maximum retention in SA was already observed at a C:Fe of 5 (i.e. surface saturation), DOC retention by CP continued to increase linearly. Variations in the relative molar UV absorbance (at 254 nm) of DOM after interaction (ϵ/ϵ_0) suggest that CP led to a more pronounced selective retention of aromatic constituents with respect to SA, particularly at lower C:Fe ratios.





The interaction between DOC and Fe oxides may influence the accessibility, and consequently reducibility of Fe-DOC systems. This can be evaluated by following the dissolution kinetics using ascorbic acid as a reducing agent. Our first results evidenced a faster dissolution of the field coprecipitate with respect to the pure amorphous Fe hydroxide, suggesting that the presence of OM on the surface or inside the substrate could actually favour dissolution by affecting the structure or by serving as a 'catalytic agent' in the reductive process (i.e. electron shuttling).

Experimental design

We tested this hypothesis by synthesizing a series of Fe-DOC systems with increasing C:Fe ratios prepared by either **surface adsorption (SA)** or **coprecipitation (CP)**. DOC was obtained by incubating rice straw in water under oxic conditions at 25°C for 30 days. Increasing amounts of DOC were equilibrated (pH = 6) with a known mass of ferrihydrite (initial molar C:Fe ratios of 1, 5 and 10) to obtain surface coated Fe-DOC systems with increasing C loading. On the other hand, coprecipitates with similar initial C:Fe ratios were obtained by the oxidation of a Fe(II) solution in the presence of increasing amounts of DOC at pH = 6. A natural Fe-DOC coprecipitate was also obtained by *in situ* sampling of a paddy soil solution from the anaerobic topsoil during a cropping season, and subsequent oxidation in the laboratory.

SUBSTRATE	Preparation	C: Fe	[Fe(II)] ₀ (mM)	[DOC] ₀ (mM)
Fh	Oxidation	-	2.0	0.0
1Fh_SA	Surface adsorption	1	2.0	2.0
5Fh_SA	Surface adsorption	5	2.0	10.0
10Fh_SA	Surface adsorption	10	2.0	20.0
1Fh_CP	Coprecipitation	1	2.0	2.0
5Fh_CP	Coprecipitation	5	2.0	10.0
10Fh_CP	Coprecipitation	10	2.0	20.0
xFh_CP	Field coprecipitate	4.3	2.0	3.6

CP kinetics showed a decrease in the rate of Fe(II) oxidation with increasing C:Fe ratios, probably due to the chelation of Fe(II) ions by DOC and the possible consumption of O_2 during the oxidation of organic functional groups. A similar trend in OH⁻ consumption was observed. The total amount of OH⁻ consumed deviated from stoichiometric values with increasing C:Fe ratios due to the high buffering capacity of the added DOM.

At the beginning of the CP process, rapid oxidation of Fe(II) and precipitation of Fe hydroxide resulted in a fast retention of DOC, and a strong selection of aromatic constituents, particularly at lower C:Fe ratios, probably by ligand exchange on the positive sites of the Fe hydroxide formed.



At later stages of CP, we observed a decrease in the affinity of precipitated Fe hydroxides for DOC. This was probably due to the previous consumption of the most reactive constituents of DOC. The slower decrease in $\varepsilon/\varepsilon_0$ values at this stage confirms this.

Conclusions

Coprecipitation may represent a key process in regulating the selective retention of important amounts of DOC in paddy soils subjected to frequent changes in redox conditions, and potentially contributing to C accumulation. However, if our further studies confirm that coprecipitation also favours the subsequent reducibility of the formed substrates, this could suggest that this process leads to the formation of a dynamic pool of labile C and Fe that is strongly influenced by redox alternations.

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