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

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Although the importance of Fe (hydr)oxides for soil organic matter (OM) stabilization and C retention by surface adsorption is well known, only recently has coprecipitation been recognized as an important process responsible for C storage in hydromorphic soils, such as rice paddy soils. Under periodic fluctuations in redox conditions the interaction between dissolved organic carbon (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 was 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. Coprecipitates sampled *in situ* also showed a similar retention of organic C confirming that this process may contribute significantly to the OM stabilization in paddy topsoils. The mechanisms involved in the retention of straw-derived DOM during coprecipitation were shown to be strongly dependent on C/Fe ratio of the solution. Although the overall coprecipitation process was highly selective for aromatic constituents, initial complexation of Fe²⁺ and precipitation as C-rich metal salts involved the selective interaction with aliphatic carboxylic constituents. The contribution of the latter mechanism to total C retention during coprecipitation was shown to increase with increasing solution C/Fe ratios. These aliphatic complexes formed during coprecipitation may play an important, though often underestimated, role in C stabilization in hydromorphic. The process-related selectivity of specific constituents of DOM during coprecipitation highlights the involvement of specific mechanisms, i.e. complexation, adsorption, salt precipitation, while ruling out non-selective, physical occlusion of OM within the forming coprecipitate.