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Influence of adsorption versus 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, and Daniel Said-Pullicino

Rice Agro-ecosystem and Environmental Research Group, Dept. of Agricultural, Forest and Food Sciences, University of Torino, Grugliasco, Italy (marcella.sodano@unito.it)

The dissimilatory reduction of Fe oxides is the main organic C-consuming process in paddy soils under anoxic conditions. The contribution of Fe(III) reduction to anaerobic C mineralization depends on many factors, but most importantly on the bioavailability of labile organic matter and a reducible Fe pool as electron donors and acceptors, respectively. On the other hand, the strong affinity of these minerals for organic matter and their capability of protecting it against microbial decomposition is well known. Natural Fe oxides in these soils may therefore play a key role in determining the C source/sink functions of these agro-ecosystems.

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. Indeed, Fe-DOC associations may not only reduce the availability of DOC, but may also limit the microbial reduction of Fe oxides under anoxic conditions. In fact, the accessibility of these minerals to microorganisms, extracellular enzymes, redox active shuttling compound or reducing agents may be impeded by the presence of sorbed organic matter. In soils that are regularly subjected to fluctuations in redox conditions the interaction between DOC and 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). However, little is known on how these processes influence DOC retention, and the structure and subsequent reducibility of these Fe-DOC associations.

We hypothesized that the nature and extent of the interaction between DOC and Fe oxides may influence the accessibility of the bioavailable Fe pool and consequently its reducibility. We tested this hypothesis by synthesizing a series of Fe-DOC systems with increasing C:Fe ratios prepared by either surface adsorption or coprecipitation, DOC was obtained by incubating a suspension of rice straw in water (straw-solution ratio of 1:30) under oxic conditions at 25˚C for 30 days to simulate the decomposition of rice straw in the field. 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 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 topsoil during a cropping season, and subsequent oxidation in the laboratory. The surface and chemical properties of all substrates were subsequently evaluated and compared. We hereby present the first results of the influence of adsorption vs coprecipitation on the selective retention of DOC, structure and surface charge, as well as their susceptibility to chemical reduction with ascorbic acid.