

The Role of Metal Redox Coupling Processes in Carbon Cycling and Stabilization

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The association of carbon with mineral phases has been increasingly recognized as a major stabilizing mechanism for protecting organic matter against microbial degradation in soils. Iron (Fe) and manganese (Mn) oxides are of particular importance because of their abundance in soils and high reactive surface area. Both Fe and Mn are susceptible to redox variability along landscape gradients. Reductive dissolution and transformation of Fe and Mn minerals governs the amount, form and transport of sequestered C. We have investigated Fe speciation as well as the composition of organic matter and its molecular interaction with soil minerals across hillslope transects within the Christina River Basin Critical Zone Observatory (CRB-CZO) to link iron-redox coupling processes with soil C cycling. Selective chemical extractions, X-ray absorption spectroscopy (XAS), micro-XAS techniques, and Mossbauer spectroscopy were employed to characterize soil Fe speciation. Applying scanning transmission X-ray microscopy (STXM) and carbon near edge X-ray absorption fine structure (CNEXAFS) spectroscopy, we mapped the spatial distribution of carbon and carbon forms, and imaged the association of organic functional groups with specific minerals in the soils. Ferrihydrite, because of its ubiquitous occurrence in the environment and its high surface area, contributes significantly to the sorption of organic matter and protects it against microbial degradation in soils and sediments. In addition, ferrihydrite often forms in the presence of dissolved organic matter in the natural environment, which leads to coprecipitation of organic matter with ferrihydrite. However, the extent and mechanisms of organic matter adsorption to or coprecipitation with ferrihydrite, and the consequences of such reactions for the properties of sorbed versus coprecipitated organic matter remain largely unknown. In this presentation, we compare adsorption and coprecipitation with dissolved organic matter from a forest litter layer. To examine the chemical fractionation of the organic matter and the mechanisms of organo-ferrihydrite complex formation associated with these two processes CNEXAFS and Fourier transform infrared (FTIR) spectroscopic techniques were employed. To study spatial distribution, macromolecular structure, and chemical composition of sorbed and coprecipitated OM at the nanometer-scale we used STXM. Data on the role of Mn in C cycling will also be presented. Such studies will enhance our understanding of OM stabilization mechanisms on soil mineral surfaces and will provide new insights on the metal-redox coupling processes affecting carbon cycling at soil/sediment-water interfaces.