The Impact of Redox Fluctuations on coupled Fe and C Cycling

CHUNMEI CHEN[1,2], DONALD L.SPARKS[2], AARON THOMPSON[1]

[1]Department of Crop and Soil Science, University of Georgia, Athens, GA. cmchen@uga.edu, aaront@uga.edu
[2]Delaware Environmental Institute, University of Delware, Newark, DE. dlsparks@udel.edu

Fe minerals play a critical role in soil C cycle by retaining organic matter (OM) or mediating OM decomposition as a resut of Fe redox cycles. Soil Fe(III) (oxyhydr)oxides serve as abundant terminal electron acceptors for anaerobic microbial growth and microbial reduction of Fe(III) in the solid phase leads to the production of Fe(II). Fe(II) under anoxic conditions can catalyze the transformation of poorly crystalline ferrihydrite (Fh) to more stable Fe minerals. The mineral-bound OM changes the mineral surface properties and the reactivity of Fh. In this study, we investigated the extent and pathway of Fe(II)-catalyzed transformation of Fh, Fh with adsorbed OM, and Fh coprecipitated OM and evaluated its subsequent consequences for C dynamics. The effects of OM types (dissolved organic matter (DOM) vs. polysaccharides) were also compared. Regardless of OM types, the difference in Fh transformation was small between the adsorbed and coprecipitated OM at similar OM loadings. DOM impeded goethite and magnetite formation and stimulated lepidocrocite formation, whereas polysaccharides did not alter the resulting secondary Fe minerals and goethite was the major secondary Fe minerals. OM remains associated with Fe minerals following Fh transformation to more stable Fe minerals, whereas Fe(II)-catalyzed Fh transformation may decrease OM stability under anoxic conditions.

In homogeneous systems, the rate of aqueous Fe(II) oxidation by O_2 governs the crystal order of the resulting Fe(III) minerals and their reactivity toward microbial Fe reduction, which is coupled with OM decomposition. But it remains unclear if this same behavior occurs in soils, where much of the Fe(II) is present as surface complexes. This study examined how the rate of Fe(II) oxidation by O_2 affects subsequent microbial Fe(III) reduction and C mineralization rates. We added isotopically-labeled ^{57}Fe(II) to soil suspensions and exposed them to 21% and 1% of O_2 for 9 d, followed by a 14 d anoxic period. We tracked the fall and rise of ^{57}Fe and measured CO_2 evolution to quantify Fe reduction rates and C mineralization rates. Mössbauer spectroscopy was used to track the solid phase Fe speciation. Our preliminary results suggest higher O_2 levels leads to fast Fe(II) oxidation followed by more rapid Fe reduction events during the subsequent anoxic cycles.