

Influence of pO₂ on iron cycling and anaerobic carbon mineralization in redox dynamic soils

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Fe oxyhydroxides play a critical role in soil C cycling by retaining organic carbon (OC) in solid-phase or mediating OC decomposition. The rates of homogeneous Fe(II) oxidation in aqueous systems by O₂ govern the crystal order of the resulting Fe(III) oxyhydroxides and their reactivity towards subsequent microbial reduction under anoxic conditions, which is coupled with anaerobic OC mineralization. It is unclear if oxidation rate exerts this control in the presence of mineral sorbents (e.g., Fe and Al oxyhydroxides) or organic matter, both of which can complex Fe(II) and alter oxidation rates and trajectory. The objective of this study was to assess how varying O₂ concentrations affects Fe(II) oxidation and its subsequent microbial Fe(III) reduction and anaerobic OC mineralization following a transition from oxic to anoxic conditions. To investigate this, we conducted several batch slurry experiments using isotopically-labeled ⁵⁷Fe(II) and either soil from the Luquillo Critical Zone Observatory or model Fe and Al oxides as sorbent surfaces. In both cases, we exposed the reactors to 21%, 1% or 0.1% O₂, followed by an anoxic incubation. Our results demonstrated that higher O₂ levels lead to faster Fe(II) oxidation and the partitioning of the amended ⁵⁷Fe into less crystalline Fe(III)-oxyhydroxide populations (based on Mössbauer analysis). To account for atom exchange and recrystallization during the experiment, we developed a numerical model to simulate the experimental data and calculated the atom exchange rate. We observe greater rates of Fe(III) reduction following the high pO₂ treatments than the lower pO₂ treatments. The anaerobic production of Fe(II) and CO₂ was well correlated, suggesting that Fe reduction was coupled to microbial OC mineralization. This study illustrated that the amplitude of O₂ fluctuations affect coupled Fe-C redox dynamics.