

Iron redox cycling: unexplored mechanisms for soil organic matter decomposition

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Iron (Fe) oxide minerals have long been known to protect soil organic carbon (C) from microbial decomposition, especially in humid tropical soils abundant in both Fe and C. In soils that experience fluctuations in oxygen (O₂) availability, however, sequential reduction and oxidation of Fe could indirectly stimulate C *decomposition* via multiple mechanisms. Reactions between O₂ and reduced Fe (Fe(II)) are known to generate reactive oxygen species and have been well-studied in the context of wastewater treatment and bioremediation, but have largely been ignored in natural ecosystems. Here we demonstrate the potential importance of Fe(II) oxidation as a mechanism for C decomposition in Puerto Rican humid tropical forest soils that naturally experience high rates of Fe reduction and oxidation. We sampled soils from multiple forest types capturing a wide range in Fe(II) concentrations (0.05 – 7.39 mg Fe g soil⁻¹) and assayed samples for phenol oxidative activity using a standard colorimetric method. To test the influence of Fe(II) oxidation on short-term CO₂ production, we amended replicate soil samples in the laboratory with concentrations of Fe(II) observed in the field, and exposed soils to either static anaerobic conditions or sequential anaerobic/aerobic conditions.

We found a strong positive correlation ($R^2 = 0.82$, $p < 0.0001$) between oxidative activity and Fe(II) concentrations within and among five humid tropical forest sites, suggesting a role for Fe(II) oxidation in C decomposition. Samples incubated under anaerobic conditions showed negligible oxidative activity, confirming the importance of O₂ for oxidation. In soils exposed to sequential anaerobic/aerobic conditions in the laboratory, Fe(II) addition stimulated CO₂ production approximately linearly with increasing Fe(II) concentration up to 270% of the control. Declines in Fe(II) and increases in HCl-extractable Fe(III) provided evidence for Fe(II) oxidation. Under static anaerobic conditions, CO₂ production did not increase systematically with increasing Fe(II) concentrations, suggesting that reactions between Fe(II) and O₂ mediated the increased CO₂ production that we observed under aerobic conditions.

Traditional models of soil C cycling posit that anaerobic conditions inhibit soil organic matter decomposition because of energetic and enzymatic constraints on microbial decomposers. Our data suggest that in Fe-rich soils Fe reduction and subsequent oxidation can stimulate C decomposition, implying that fluctuating O₂ environments could generate higher rates of C loss than would be predicted by summing rates derived under static aerobic or anaerobic conditions. Incorporating redox cycling in biogeochemical models could provide important explanatory power.