

Oxic-Anoxic Interfaces in Soils and Sediments: Hotspots of Manganese-driven Carbon Oxidation

MARCO KEILUWEIT^{1*}, PETER NICO², MALAK TFAILY³,
JÜRGEN THIEME⁴, TOM REGIER⁵, AND MORRIS JONES¹

¹ University of Massachusetts Amherst, Amherst, MA, USA
(*correspondence: keiluweit@umass.edu)

² Lawrence Berkeley National Laboratory, Berkeley, CA,
USA

³ Pacific Northwest National Laboratory, Richland, WA, USA

⁴ Brookhaven National Laboratory, Brookhaven, NY, USA

⁵ Canadian Lightsource, Saskatoon, Saskatchewan, Canada

The formation of reactive manganese (Mn) species is emerging as a key regulator of carbon oxidation rates, and thus CO₂ emissions, in soils and sediments. Although reactive Mn species are among the most potent oxidants in environmental systems, the controls on Mn-driven carbon oxidation are virtually unknown. Understanding the influence of Mn redox dynamics on carbon oxidation rates is critical to predicting future soil CO₂ emissions and their impact on the climate system. Many soil and sediment environments are characterized by steep oxygen gradients, forming oxic-anoxic transitions that enable rapid redox cycling of Mn. Here, we aimed to identify the impact of Mn(II) oxidation along oxic-anoxic transitions on carbon oxidation rates. To accomplish this objective, we induced well-defined oxygen gradients within forest soil using laboratory-based diffusion reactors. Electrochemical and spectroscopic analyses showed that C depolymerization and oxidation was greatest at the oxic-anoxic interface, and was proportional to the rate of Mn(II) oxidation. X-ray microprobe imaging further revealed that enhanced C oxidation at the interface was directly linked to the formation of reactive Mn(III) phases. Characterization of both proteomes and lipidomes across the redox profile, in combination with control experiments to inhibit fungi and/or bacteria, further established that Mn(III) generation at the interface is mediated through fungal oxidative enzymes. Combined, our findings demonstrate that oxic-anoxic interfaces in soils represent hotspots of C oxidation, which rely on fungal Mn cycling to produce reactive Mn(III) species. Our results suggest that we should regard C oxidation rates not merely as a function of molecular composition, which insufficiently predicts rates, but in relation to microenvironments favoring the formation of critically important oxidants such as Mn(III).