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Microbes drive manganese(III)-mediated organic matter degradation at redox interfaces

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The formation of trivalent manganese (Mn) has recently been demonstrated to be a critical driver of organic matter degradation in soil environments, regulating nutrient cycling, CO_2 emissions, and ultimately impacting soil carbon storage. Recent evidence suggests that oxic-anoxic interfaces – ubiquitous in most soil environments – act as hotspots for reactive Mn(III) formation. However, the microbial drivers of Mn(III) formation in soils as well as their impact on oxidative organic matter degradation remain largely unknown. Here we show that organic matter degradation is tightly coupled to the enzymatic formation of Mn(III) along oxic-anoxic interfaces in soils. To do so, we established stable redox gradients in diffusion reactors packed with forest soils of varying Mn availability for a 12-week incubation, and monitored changes in microbial dynamics, Mn transformation, and organic matter degradation. Over the course of the experiment, CO_2 production was positively correlated with Mn(II) availability, Mn(II) oxidation rates, and fungal:bacterial ratio, suggesting a direct link between fungal Mn(II) oxidation and organic matter degradation. Wet-chemical and X-ray spectroscopic analyses further revealed significant hotspots of Mn(III) production concentrated along the oxic-anoxic interfaces. Mn(III) formation at the interface increased with enhanced soil Mn(II) availability and was significantly correlated with the expression of genes coding for oxidoreductases, particularly those with putative Mn(II)-oxidizing potential. Moreover, gene expression of oxidoreductases was significantly correlated to measured phenol oxidative potentials, pointing to a direct link between the activity of Mn(II)-oxidizing enzymes and organic matter degradation. Together, our results indicate a tight coupling between enzymatically-catalyzed formation of reactive Mn(III) species and microbial organic matter degradation at oxic-anoxic interfaces. These findings provide a first characterization of enzymatic pathways involved in Mn(III) production in soils, yielding critical mechanistic information regarding the source of oxidative capacity for organic matter degradation in redox-active soil environments.