

## Coupled biotic-abiotic oxidation of organic matter by biogenic MnO<sub>2</sub>

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Some reactive soil minerals are strongly implicated in stabilising organic matter. However, others can play an active role in the oxidation of organic molecules. In natural systems, layer-type manganese oxide minerals (MnO<sub>2</sub>) typically occur as biomineral assemblages consisting of mineral particles and microbial biomass. Both the mineral and biological fractions of the assemblage can be powerful oxidants of organic C. The biological compartment relies on a set of enzymes to drive oxidative transformations of reduced C-substrates, whereas MnO<sub>2</sub> minerals are strong, less specific abiotic oxidants that are assumed to rely on interfacial interactions between C-substrates and the mineral surface. This project aims to understand the coupling between microbial C mineralization and abiotic C oxidation mediated by MnO<sub>2</sub> in bacterial-MnO<sub>2</sub> assemblages. Specifically, under conditions of high C turnover, microbial respiration can significantly alter local pH, dissolved oxygen and pool of available reductants, which may modify rates and mechanism of C oxidation by biotic and abiotic components.

We first investigated changes in the solution chemistry of *Pseudomonas putida* suspensions exposed to varying concentrations of glucose, chosen to represent readily bioavailable substrates in soils. Glucose concentrations tested ranged between 0 and 5.5mM and changes in pH, dissolved oxygen and dissolved organic and inorganic carbon were tracked over 48h. We then combined literature review and wet-chemical experiments to compile the pH dependence of rates of organic substrate oxidation by MnO<sub>2</sub>, including glucose. Our results demonstrate a strong pH dependence for these abiotic reactions. In assemblages of *P. putida* - MnO<sub>2</sub>, kinetic limitations for abiotic C oxidation by MnO<sub>2</sub> are overcome by changes in biogeochemical conditions that result from bacterial C metabolism. When extrapolated to a soil solution confronted to an input of fresh dissolved organic matter, bacterial C metabolism of the labile fraction may lower solution pH into a regime that favours abiotic oxidation of recalcitrant C by MnO<sub>2</sub>. This project demonstrates that the co-occurrence of mineral particles with metabolically active cells provides a direct link between the C and Mn cycles.