Goldschmidt 2022 Abstract
https://doi.org/10.46427/gold2022.12766

Electron flows in bacteria-birnessite composites and implications for soil carbon oxidation

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The biogeochemical cycling of manganese (Mn) can influence ecosystem carbon (C) dynamics through multiple pathways. For instance, reactive manganese oxide phases such as layer-type manganese oxides can increase the pool of accessible C substrates in soil by promoting the decomposition of organic molecules into smaller fragments through hydrolytic or oxidative mechanisms. However, the current literature is sparse with respect to the mechanism through which oxidized Mn species (i.e., Mn(III, IV)) species transform OM and the extent to which these redox transformations impact microbial carbon metabolisms and thus soil carbon oxidation.

In the current study, we investigated how redox-reactive Mn oxide phases impact carbon cycling in model organo-microbe-mineral composites formed by glucose, *Pseudomonas putida (P. putida)*—a common soil and rhizosphere bacterium, and δ-MnO_2. We performed kinetic experiments over a 144 h at pH 5 and 7 to identify the extent and mechanism of glucose by δ-MnO_2 incubations. Subsequently, we compared the oxidation and assimilation of glucose in bacteria-only and bacteria-mineral incubations. Kinetic experiments were accompanied by wet-chemical measurements of C and Mn chemistry, bacterial growth, respiration and stable C isotope analysis of the bacterial biomass and respired CO_2. These measurements were integrated to examine changes in the allocation of carbon between biomass building, extracellular secretions and respiration in response to the abiotic oxidation of glucose by δ-MnO_2.

Our results showed that the abiotic oxidation of glucose did not produce CO_2 but instead generated formate. This abiotically-produced formate underwent dissimilatory oxidation in bacteria-mineral systems, as demonstrated through isotopic analysis of the respired CO_2. Additionally, the co-utilization of glucose and formate by *P. putida* enhanced dramatically the secretion of gluconate and 2-ketogluconate, with 60 % of the carbon added as glucose appearing as gluconate and 2-ketogluconate after 24 h of incubation. Beyond 24 h, the bacteria entered a non-growing state and showed limited recycling of the secreted metabolites, in contrast to bacteria-only incubations. Overall, our research shows that redox-sensitive minerals like manganese oxides can lower carbon use efficiency through direct and indirect transformations of organic carbon molecules in soil and rhizosphere environments.