Coupled dynamics of carbon and manganese: Influence of organic compounds on reactivity of biogenic Mn oxides

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Manganese oxides are one of nature's most potent oxidants and, due to their ubiquitous nature in soils and sediments, play a critical role in the cycling of redox-active trace metals and contaminants. While these oxides also bear an important control on soil carbon cycling, it remains unclear how carbon species present during biogenic manganese oxidation can affect the structure and reactivity of these bio-oxides. The reaction between Mn(IV) and organic compounds/extracellular polymeric substance (EPS) can generate Mn(III), modifying the reactivity of Mn oxides. In addition, the proportion of Mn(III) hosted within these oxides can influence the number of reactive cation vacancies in MnO_2 sheets thus impacting metal sorption capacity.

In this study, we investigate electron transfer reactions between abiotic and biogenic Mn oxides and organic compounds. We synthesized abiotic δ-MnO_2 and developed a protocol to produce biogenic Mn oxides in the absence of an organic buffer. Next, we added 10 mM HEPES buffer, historically assumed to be biochemically inert, to a range of abiotic and biogenic Mn-oxides and monitored Mn(III) content over time. Average manganese oxidation numbers (AMON) and Mn(III) content were determined by a three-step potentiometric titration and with a pyrophosphate extraction, respectively. Total digested Mn and aqueous Mn(II) concentrations were measured by inductively coupled plasma optical emission spectrometry.

Our results show that organic carbon species exert a strong control on Mn oxide reactivity. Biogenic manganese oxides precipitated by *P. putida* both in the presence and absence of HEPES showed different initial amounts of Mn(III). In both treatments, Mn(III) content increased over time following the addition of HEPES. However, in the presence of glucose, a readily available carbon source for *P. putida,* Mn(III) content doubled within the first hour of the HEPES addition but then significantly decreased. Understanding the cycling of Mn(III) within biogenic oxides in relation to carbon metabolism will increase our understanding of Mn oxide mineralization in soils and shed insight into the control of organic carbon species on Mn oxide structure and oxidation state within the environment.