

Biogenic Mn oxide influences on metal(loid) contaminants

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The distribution and speciation of manganese (Mn) in terrestrial and aquatic environments is heavily influenced by microbiological processes as well as environmental factors (solution chemistry, pH, redox potential, etc). A diversity of microorganisms (bacteria, fungi, and algae) contribute to Mn(II) oxidation in aerobic environments, which results in the formation of sparingly soluble Mn(III/IV)(hydr)oxide minerals. Biogenic Mn oxides typically exist as sheet structures with varying Mn(III/IV) contents and vacancies. These structural and chemical properties exert control over the reactivity of Mn oxides, greatly influencing the fate and distribution of nutrients and contaminants through adsorption, coprecipitation, and redox reactions. While abiotic Mn oxide mineral structures and reactivities have been well studied, substantial differences in Mn biominerals can alter interactions with trace metal(loids) that require greater examination under a range of environmental conditions.

In controlled laboratory experiments, we have examined Mn oxides produced by a variety of environmentally relevant eukaryotic Mn(II)-oxidizing microorganisms (fungi and algae) as well as the reactivity of these biominerals towards different trace metals and metalloids. In these experiments, biogenic Mn oxides behave differently than abiotic minerals. For example, structural incorporation and adsorption of Ni to biogenic Mn oxides is approximately equal regardless of the timing of Ni exposure (during or after mineral exposure), whereas these exposure effects do influence Ni binding to abiotic phyllophanates. Furthermore, certain fungi capable of simultaneously precipitating Mn oxides and Se(0) nanoparticles yield unexpectedly stable forms of both minerals – the Se(0) does not appear to re-oxidize despite being in direct contact with the strongly oxidizing biogenic Mn oxides. These and other studies looking at the reactivity of Co, Ni, Cu, and Zn under saline conditions further demonstrate the uniqueness of these highly reactive biogenic mineral phases under a variety of environmental conditions.