Mycogenic Biogeochemistry: Simultaneous Manganese Oxidation and Selenium Reduction in Oxic Systems

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Manganese (Mn) and selenium (Se) are two dynamic, redox sensitive, trace elements that play important roles in human and ecosystem health. In natural systems, Mn oxides can greatly impact the fate and transport of contaminants and nutrients by acting as oxidants of organic compounds and redox-sensitive elements, and/or as a sink for contaminants. Selenium, which is both a nutrient and contaminant with a very small window of sufficiency, can have detrimental ecological impacts owing to its toxicity at high concentrations. Of particular interest for mitigating negative ecological effects of Se, is the ability of fungi to reduce aqueous Se(IV or VI) to nanoparticulate Se(0) and organic Se(-II) in oxic conditions, though the long-term stability and reactivity of these reduced forms is currently unknown.

We investigated biogeochemical products of two common environmental fungi during growth in the presence of Mn(II) and Se(IV or VI). Both fungi are capable of individually oxidizing Mn(II) to Mn(III/IV) oxides and aerobically reducing Se(IV or VI) to Se(0 and/or -II). Fungi were grown in oxic conditions containing 100 uM Mn(II) and 100 uM Se(IV or VI) for one month. When grown in the presence of both Mn and Se (IV or VI), the fungal species maintain their capacity for aerobic Se reduction, effectively removing Se from overlying oxic solutions, while simultaneously producing Mn oxides (triclinic and hexagonal birnessite-like phases). We used X-ray absorption spectroscopy to investigate the solid-associated Se, which is dependent on starting Se speciation, and is unexpectedly stable despite its direct contact with the strongly oxidizing Mn oxides. During growth with Se(IV), fungi produce 50% Se(0) and 50% organic Se(-II), while nearly 100% of the products from fungal growth with Se(VI) are organic Se(-II). Mycogenic biogeochemical processes offer a route for mitigating negative ecological impacts of Se by forming stable products with limited mobility and bioavailability.