

Shifts in Iron and Manganese Oxidation States, Bonding Environments, and Mobility in Mining-Impacted Lake Sediments Exposed to Anoxic and Anoxic + Algal Detritus Experimental Conditions

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In metal-contaminated Lake Coeur d'Alene in northern Idaho (US), seasonal stratification and redox processes control the mobility of metals and their release from mining-impacted sediments into the water column. An estimated 75 million tonnes of metal-rich sediments, including 470,000 tonnes of Pb, along with substantial masses of As, Cd, Fe, Mn, Zn, and associated S, were discharged into the lake over the past 100+ years. Future conditions of the lake are expected to include deposition of algal detritus to the sediment-water interface that may alter metal remobilization during the seasonal euxinic environment. Cores of the lake sediments were exposed to anoxic and anoxic + algal detritus conditions for eight weeks at 4 °C. At a location below the sediment-water interface, anoxic conditions promoted a shift in S species to continually larger concentrations of reduced species and anoxic+ algal detritus conditions suppressed the increasing trend of reduced S species. These algae-induced redox changes in this metal-rich zone (Fe ~10% and Mn ~2%) caused greater release of Mn early in the experiment compared to the anoxic-only conditions but did not appear to alter the release of As, Cd, or Fe. This dissimilatory metal reduction process was examined by comparing changes in sediment Fe and Mn oxidation states and bonding environments through synchrotron X-ray spectroscopy. Results indicate that organic matter oxidation induces an early electron acceptor preference and enhanced mobility of Mn with the algal detritus input. Algal oxidation appears to shift the early changes in metal oxidation states and complexation (bonding environment), but redox conditions and metal release become similar between the two experimental conditions by the end of the 8-week period. It is likely that the availability of Mn⁴⁺ as an Fe (oxyhydr)oxide sorbed species makes it readily available for reduction and is available for release into solution because of low complexation with reduced S compared to Fe.