

Reduction of Hg^{II} by Mn^{II}

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The reduction of Hg^{II} to Hg⁰ can occur via both abiotic and microbial mediated processes; therefore, in addition to direct microbial reduction, abiotic reduction is a key component of global Hg biogeochemical cycling. Reduction of Hg by Fe^{II} (mixed Fe^{II/III} mineral phases, Fe^{II} sorbed to minerals, and aqueous Fe^{II}) has gained significant attention in the past few years.

Manganese (Mn) is Earth's second most abundant transition metal next to Fe and resembles iron in several aspects of its geochemistry. Oxidation of Mn^{II} to Mn^{III} and Mn^{IV} is largely driven by microorganisms. In addition, recent studies have shown the importance of mineral surface-catalyzed Mn^{II} oxidation, which can influence Hg^{II} reduction. Reduction of Hg^{II} to Hg⁰ is thermodynamically favored during coupled oxidation of Mn^{II} to Mn^{III/IV} at pH 7 and above. However Mn^{II} has never been documented to reduce Hg^{II} to Hg⁰.

Here, we evaluated the potential of Mn^{II} to reduce aqueous Hg^{II} by characterizing the solid-phase Hg and Mn species with synchrotron X-ray Absorption Spectroscopy (XANES and EXAFS). Solution phase activity of Hg and Mn was monitored using ICP-AES. We find that the redox reactivity, the reaction pathways, and the resulting Hg speciation strongly depend on pH, presence of complexing ligands, and surface area of minerals.

At pH 7.5, the majority of Hg^{II} was reduced to Hg⁰ within hours. Hg^{II} reduction was coupled with oxidation of soluble Mn^{II} to highly insoluble Mn^{IV} oxide. Formation of a Mn^{IV} oxide mineral auto-catalyzes the reaction for first few hours, followed by significantly slower rate of reaction concomitant with changes in Mn^{IV} mineral phase. The presence of inert mineral surfaces (e.g. Al₂O₃ and TiO₂) inhibited the rate of Hg^{II} reduction. Hg^{II} reduction by Mn^{II} results in the formation of meta-stable Hg^I species in the presence of complexing ions such as sulphate, which slowly transforms to Hg⁰ over an extended period of time. Since Mn^{II} can exist at up to millimolar concentrations in natural waters, Mn could have important implications on the overall mobility and bioavailability of Hg. Mn oxides, which are strong oxidants, likely re-oxidizes Hg⁰; with Mn playing a dual role of reductant as well as oxidant of Hg in natural systems.