Redox Manipulation: A Novel Approach for In Situ Remediation of Mercury Contaminated Sediments

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Environmental risk at mercury (Hg) contaminated sites derives mainly from methylmercury (MeHg) exposure and bioaccumulation. MeHg is produced by heterotrophic bacteria that use sulfate, iron, and CO_2 as terminal electron acceptors (TEA). Our research is focused on mineral-based amendments that can serve as a preferred alternate TEA to inhibit sulfate reduction, thereby suppressing mercury methylation in situ. Manganese(IV) oxides (pyrolusite and birnessite), applied either as direct sediment amendments or in a thin-layer reactive cover, have been demonstrated to reduce net MeHg production and efflux (by an order of magnitude) from contaminated sediment in laboratory sediment-water "aquarium" microcosms operateed for several months. Microbial community census using PCR and DNA sequencing indicates that the addition of manganese oxide does not markedly alter the indigenous community structure although an increase in iron and manganese reducing species was observed. The mechanism of MeHg suppression therefore most likely involves a shift from sulfate reduction to Mn(IV) reduction as the energetically favorable TEAP. CO_2 respirometry shows no evidence of microbial toxicity of the amendments but rather suggests that the Mn(IV) addition actually stimulates microbial activity. Mn XANES shows that Mn(IV) oxides are gradually converted to mixed-valence Mn(II/III) oxides (e.g. bixbyite, hausmanite) and rhodochrosite over time, a solid phase assemblage which continues to poise redox and inhibit sulfate reduction, and thereby suppress Hg methylation. The retention of the added Mn in the sediment also suggests an area for future work -- the possibility for regeneration of Mn(IV) oxides under dynamic settings where soils and sediments experience periodic redox fluctuations (e.g. subaerial exposure due to tidal cycles in intertidal zones and marshes), thereby prolonging amendment effective lifetime, and providing for sustained in situ suppression of MeHg production.