Suppression of Methylmercury in Sediments by Manganese(IV) Oxide

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Environmental risk from Hg-contaminated sediments is due primarily to methylmercury (MeHg) exposure and bioaccumulation. Reducing MeHg concentrations as a means of risk reduction *in situ* can therefore be an appropriate target for remediation. MeHg levels in sediments and porewater reflect a balance between Hg methylation and MeHg demethylation, both of which are microbially mediated processes. MeHg production in aquatic sediments is generally associated with specific terminal electron accepting processes (TEAPs) including sulfate reduction, Fe(III) reduction and methanogenesis, while demethylation can occur by both oxidative and reductive pathways [1,2]. We hypothesize that manipulating sediment redox with a solid-phase amendment (pyrolusite, MnO_2) to set and maintain Mn(IV) reduction as the dominant TEAP can inhibit Hg methylation and enhance MeHg degradation in Hg-contaminaed sediments.

In anaerobic sediment-water microcosm tests with a contaminated estuarine sediment (95 ug/g total Hg), average dissolved MeHg concentrations were 92% lower (0.12 ng/L) in pyrolusite-amended micorcosms than in live control (unamended) micrcosms after 16 weeks incubation, while total dissolved Hg concentrations were not significantly different. Monitoring of redox indicators (Eh, dissolved Fe, Mn, sulfide) confirmed that the amended systems were poised at Mn(IV) reduction while controls ultimately went sulfidic. Spiking sediment microcosms with soluble inorganic Hg ($HgCl_2$ solution) greatly enhanced average dissolved MeHg in live controls after 2 weeks (101 ng/L) while amended microcosms remained essentially unchanged at 0.40 ng/L. Pyrolusite also reduced total dissolved Hg by ~80% likely due to adsorption of Hg chloride complexes. In another experiment, synthetic MeHgCl solutions were reacted with commercial pyrolusites covering a range of grain size and purities. Dissolved MeHg concentrations were reduced by up to 95% after 1 hour, with demethylating activity apparently increasing with both specific surface area (finer grain size) and higher impurity content.

[1] Hsu-Kim *et al* (2013) *Environ. Sci. Tech.* **47**, 2441-56 [2] Gilmour *et al* (2013) *Environ. Sci. Tech.* **47**, 11810-20