# Bioavailability and Methylation Potential of Mercury in Contaminated Sediments

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Mercury contamination in aquatic environments presents a public health risk due to microbial production of methylmercury (MeHg), a neurotoxic and highly bioaccumulative compound. Because of the hazards associated with MeHg bioaccumulation, the presence of mercury in contaminated sediments is often a driver of risk at these settings. However, remedial action can be difficult to implement due to the lack of methods to determine mercury methylation potential in sediments. Our research attempts to address this need through investigations of the chemical speciation of mercury in benthic settings and bioavailability or inorganic Hg for anaerobic microbes that produce MeHg. Laboratory experiments with sediment microcosms were performed to demonstrate that microbial production of MeHg was not simply linked to the amount of dissolved Hg or the dissolved Hg speciation as predicted by equilibrium speciation models. Rather, an enhanced production of MeHg was observed when the microcosms were exposed to nanoparticulate forms of mercuric sulfides (HgS) rather than bulkscale HgS. These experimental data were used to develop a kinetic model of methylmercury production by incorporating rates of dissolved Hg complexation, HgS precipitation, and HgS dissolution into a framework that links Hg speciation and methylation. This model indicates that a larger dissolution rate of nanoparticulate HgS compared to bulk HgS could partly explain the enhancement of MeHg production. However, another process must also be involved, such as direct uptake of nanoparticles or immediate uptake of Hg dissolving from nanoparticles, to simulate the experiment data. We used this information to explore methods to assess the bioavailability of mercury in complex matrices. These efforts include the development of a thiol-leachable Hg measurement for sediments, where a thiol ligand is used as a proxy for a biotic ligand associated with methylating bacteria. We also tested diffusive gradient in thin-film (DGT) samplers to determine how dissolved and nanoparticulate forms of Hg may differ in response to these passive samplers. These studies aim to utilize recent advances in the understanding of mercury sulfide geochemistry as a basis for methods to quantify Hg methylation potential in contaminated sediments.