Assessment of the Bioavailability and Methylation Potential of Mercury Sulfides with Sediment Slurry Experiments

University-Led Research

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In the natural aquatic environment, neurotoxic methylmercury (MeHg) mainly originates from anaerobic microbes that methylate inorganic forms of mercury in sediments. MeHg production rates can vary widely across aquatic ecosystems, sometimes by orders of magnitude. Accurate prediction of mercury methylation potential in the environment has remained elusive, partly because the mechanisms by which anaerobic microbes take up and methylate mercury are not well known. The overall goal of our research is to establish a quantitative relationship between the geochemical speciation of mercury in sediment pore water and the bioavailability of mercury to the methylating bacteria. In our previous work with pure cultures of sulfate reducing bacteria (SRB), we have demonstrated that the availability of mercury for methylation decreased during aging of mercury in sediments, a process in which mercury is expected to transform from dissolved Hg-sulfides to nanoparticulate and microparticulate forms of HgS.

To better capture the complexity of real sediment systems, we performed sediment slurry microcosm experiments to investigate the aging effect on the availability of Hg for methylation. For our slurries, we selected sediments and water at two locations in the San Francisco Bay-Delta estuary (California, U.S.A.) to represent sediments in freshwater and saline settings. The slurries were amended with one of the three forms of mercury: dissolved $Hg(NO_3)_2$ freshly mixed with Na_2S, HgS nanoparticles (<30 nm), and HgS microparticles (>1000 nm). In these HgS treatments, we compared the net MeHg production and other water quality parameters relative for Hg speciation. Our results showed that SRB were predominantly responsible for mercury methylation and their activity and subsequent MeHg production could be limited by the supply of sulfate and/or labile organic carbon. In the presence of abundant sulfate and carbon source, the bioavailability of Hg was the limiting factor for microbial methylation. The net MeHg production in the slurries amended with $Hg(NO_3)_2$+Na_2S was found to be the largest of the three types of Hg treatments, similar to our previous experiments with SRB in pure culture. Likewise, the methylation potential of nano-HgS was higher than that of micro-HgS. Nevertheless, the chemistry in natural sediments is more complex than that found in pure cultures of bacteria. Partitioning of Hg to bulk-scale mineral particles and colloids (especially FeS) may considerably influence the speciation of mercury and MeHg production. As a result, dissolved Hg in the bulk porewater (i.e., Hg remained in the supernatant after ultracentrifugation) in sediment pore water may not accurately represent the available fraction of Hg for methylation. Additional approaches targeting the Hg species that are likely taken up by the methylating bacteria (e.g., Hg-thiol complexes) are needed to assess the Hg availability in natural samples.