Nanoscale Mercury Sulfide-Organic Matter Interactions: Implications for Mercury Methylation Potential in Sediments

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Mercury contamination of soil and sediment is a concern at several Department of Energy facilities due to the long-term risks for human exposure. In sediments, anaerobic bacteria (mainly sulfate reducers) are capable of converting inorganic forms of mercury to methylmercury, a highly bioaccumulative form of the metal. One factor controlling the production of methylmercury (MeHg) is the chemical speciation of inorganic Hg in sediments (e.g., Hg-sulfides) and the amount of mercury that is bioavailable to methylating bacteria. Our previous work has demonstrated that nanoparticulate forms of $HgS_{(s)}$ can be an important portion of mercury in sediments, particularly in locations containing dissolved organic matter (DOM) that facilitates the stabilization of nanoparticles in porewater. This research aims to develop a framework for linking mercury speciation to methylation potential in sediments. The objectives are to characterize the structure and reactivity of nanoscale compounds formed during the precipitation of HgS in DOM-containing water and then relate these properties to their bioavailability to methylating bacteria.

In the first part of this work, we performed precipitation experiments in solutions containing Hg, sulfide, and dissolved humic acid. These mixtures resulted in aggregates of nanoparticles (~3 to 4 nm) with metacinnabar-like mineralogy. Pure cultures of sulfate reducing bacteria were then exposed to these nanoparticles and also to bulk scale HgS. The experiments demonstrated greater amounts of MeHg production in cultures exposed to nanoparticles than in cultures exposed to the same concentration or the same surface area of microscale $HgS_{(s)}$ particles. These results indicated that the nanoparticles provided an extra source of bioavailable mercury (perhaps via enhanced dissolution rates of nanoparticles relative to microscale particles). The methylation experiments also showed that the methylation potential of nanoparticles decreased with the 'age' of the original nano-HgS stocks.

We utilized a wide variety of tools to assess changes to the size and crystallinity of HgS nanoparticles in their original stock solution. Measurements of monomer diameter and crystallite diameter by TEM and X-ray diffraction did not show large changes over 1 to 7 days. However, small angle X-ray scattering data suggested that the Hg-S-humic acid mixtures initially comprised of small scattering units (~1 nm) that would correspond to multinuclear Hg-S cluster type compounds in solution. Small clusters or amorphous particles would not be detected in TEM or XRD analysis. These small scattering units disappeared over one day as the HgS particles ripened and aggregated in solution. We also employed extended X-ray absorption spectroscopy to investigate the short-range order of HgS species in these mixtures. Our preliminary data suggest that the particles consisted of metacinnabar-like structure. However, Hg-S coordination numbers were less than bulkscale metacinnabar, indicating the presence of nanoscale HgS particles or clusters in the sample. Overall, the characterization of the nanoparticle stock solutions demonstrated that the smallest entities (e.g., HgS cluster compounds) may have some bioavailability to methylating bacteria (perhaps via dissociation directly outside the cell membrane surface prior to uptake). The next steps will be to apply models to the SAXS and EXAFS data and extract quantitative information regarding particle size distribution. We hope to apply the results to an overall framework that can link the kinetics of Hg-S-DOM transformations to mercury methylation rates in sediments.