Nanoscale Mercury Sulfide-Organic Matter Interactions: Practical Applications for Environmental Risk Assessment

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The geochemical speciation of mercury (Hg) is an important factor that controls the bioavailability of this metal to anaerobic microorganisms responsible for methylmercury production in the aquatic environment. In anaerobic settings, Hg is largely associated with sulfides and natural organic matter (NOM). These interactions involve a variety of species, including Hg complexes with thiolate moieties on NOM and HgS nanoparticles that can be stabilized in solution by NOM coatings. This study aims to delineate how the molecular structure of NOM-coated HgS nanoparticles alters the bioavailability of Hg for methylating microorganisms and to use this information for new methods to quantify Hg bioavailability in sediments and other geomedia.

A variety of spectroscopic techniques was used to delineate the structure of HgS nanoparticles as they aged for up to one week in the presence of NOM. These nanoparticles were then amended to cultures of methylating bacteria. The results demonstrated that the methylation potential of HgS decreased with the age of the nanoparticles, and that this trend coincided with an increase in aggregation and crystallinity of the nanoparticles. The amount of dissolved Hg in solution (defined by the fraction passing a 0.02-micron filter or remaining in suspension after ultracentrifugation) was not a good predictor of Hg bioavailability. Instead, bioavailability correlated with the fraction of particulate Hg that dissolved in the presence of glutathione, a thiolate ligand that could be representative of metal binding sites on the bacterial cell envelope. These observations have been used to develop a thiolate-based selective extraction assay for quantifying metal bioavailability in geomedia. Overall, the results of this work suggest that a portion of solid-bound mercury is bioavailable to microorganisms, the reactive fraction depends on the nanoscale structure of HgS, and this fraction can be approximated by a selective extraction assay that can sufficiently mimic processes at microbe-mineral interfaces.