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Transformations of Mercury, Iron, and Sulfur During the Reductive Dissolution of Iron-oxyhydroxide by Sulfide

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Methylmercury can accumulate in fish to concentrations unhealthy for humans and piscivorous birds. Most sources of mercury (Hg) emit inorganic species to the environment. Therefore, ecological harm occurs when inorganic Hg is converted to methylmercury. Sulfate- and iron-reducing bacteria methylate Hg. Processes promoting the potential bioavailability of inorganic Hg under conditions in which these bacteria live are poorly understood. Here we show that sulfide initially decreases the concentration of dissolved and adsorbed Hg in the presence of iron-oxyhydroxide (Figure 1), forming HgS (Figure 2). However, sulfide-promoted dissolution of iron-oxyhydroxide eventually dissolves HgS via formation of ferrous iron-bearing species [Fe(II)] (Figure 1). Our results demonstrate that HgS is much less recalcitrant in the presence of Fe(II) compared to sulfide. The formation of HgS in Hg-contaminated wetland or marine sediments may not effectively limit bioavailability under conditions that promote the activity of iron-reducing bacteria. Our results emphasize the importance of considering iron in addition to sulfur speciation to effectively predict whether processes promoting Hg bioavailability are likely to dominate. Sulfur and iron speciation are useful geochemical indicators of ecological risk posed by Hg.

Figure 1 Concentrations of dissolved Hg (left axis), Fe(II), and S(II) (right axis) during sulfide addition at a normalized rate of 2.8 μM -sulfide m^{-2} -goethite surface area h^{-1} . The unit of the x-axis is an estimated mole-ratio of sulfide to goethite surface sites, assuming a constant goethite surface area of 90 $\text{m}^2 \text{g}^{-1}$ and a site density of 6 sites nm^{-2} .

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Figure 2 Phase-distribution and solid-phase molecular speciation (right axis) of mercury during sulfide addition at a normalized rate of $0.6 \mu\text{M-sulfide m}^{-2}\text{-goethite surface h}^{-1}$. See the caption of Figure 1 for an explanation of the x-axis unit.

Methods

A stirred flow reactor was utilized to apply sulfide concentration gradients (0.6 and $2.8 \mu\text{M m}^{-2} \text{h}^{-1}$) to 5 g L^{-1} goethite suspensions onto which $0.2 \mu\text{mol-Hg m}^{-2}$ was adsorbed at $\text{pH } 7.4 \pm 0.1$. The reactor was purged with nitrogen and samples were taken into a glass syringe, closed, and processed in a 2% hydrogen+98% nitrogen-filled glove bag. Dissolved constituents were defined as those capable of passing $0.2 \mu\text{m}$ filters. Dissolved Hg was measured using cold vapor atomic fluorescence spectroscopy (USEPA Method 1631). Dissolved ferrous iron [Fe(II)] was analyzed using the ferrozine assay. Dissolved sulfide was measured using the methylene blue colorimetric assay. The speciation of Hg in the solid phase was investigated using extended X-ray absorption fine structure (EXAFS) spectroscopy at the Hg L_{III} edge at the Advanced Photon Source, Argonne, Illinois, USA. Particles for EXAFS analysis were mounted on polyethersulfone membranes, dried under 2% hydrogen+98% nitrogen, and sealed in Kapton film.