

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 other predatory mammals. 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 (SRB and FeRB) methylate Hg, but the effects of processes involving oxidized and reduced forms of sulfur and iron on the potential bioavailability of inorganic Hg are poorly understood. Under abiotic conditions, using a laboratory flow reactor, bisulfide was added at 40 to 250 $\mu\text{M h}^{-1}$ to 5 g L⁻¹ goethite ($\alpha\text{-FeOOH}$) suspensions to which Hg(II) was adsorbed (30 to 100 nmol m⁻²) at pH 7.5. Dissolved Hg initially decreases from 10³ or 10⁴ (depending on initial conditions) to 10⁻¹ nM, during which the concentration of Hg(II) adsorbed to goethite decreased by 80% and metacinnabar ($\beta\text{-HgS}$) formed, according to Hg L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectroscopy. The apparent coordination of oxygens surrounding Hg, measured with EXAFS, increased during this period, suggesting desorption of monodentate, inner sphere (IS) bound Hg while bidentate, IS Hg persisted on the goethite surface. Further sulfidation increased dissolved Hg concentrations by one to two orders of magnitude (0.5 to 10 or 30 nM), suggesting that ferrous iron formed by sulfide-promoted dissolution of goethite either desorbed Hg or dissolved $\beta\text{-HgS}$. Rapid accumulation of Fe(II) in the solid phase (up to 40 $\mu\text{mol g}^{-1}$) coincided with faster elevation of dissolved Hg concentrations. A secondary Fe-bearing phase resembling poorly formed green rust was observed in sulfidized solids with scanning electron microscopy. These results suggest that surface-bound or mineralized Fe(II) strongly affects Hg speciation and therefore may affect Hg bioavailability under conditions where Fe(III) is reduced. Examination of interrelated processes involving sulfide and Fe(III) revealed new modes of Hg solubilization previously not considered in Hg methylation models.