

Mercury(II) Sorption to Fe- and Al-(Hydr)oxides: pH and Ligand-Variable Systems

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Introduction

Mercury contamination in aquatic systems is an issue of global concern and is of particular importance in areas of former mercury ore mining and industrial mercury release in wastewater. The primary mode of mercury transport from such point sources is surface and/or rainwater mobilization of mercury-bearing particles and dissolved aqueous mercury. Removal of mercury from the aqueous phase can occur through sorption to sediment particle surfaces, incorporation of mercury into precipitates, and sedimentation of mercury-bearing particles. These processes are all impacted by changes in the aquatic chemistry of the system in which mercury is being transported. The objectives of this study are to use extended X-ray absorption fine structure (EXAFS) spectroscopy to directly characterize the sorption/precipitation reactions taking place between mercury(II) and various Fe- and Al-(hydr)oxide substrates, and to investigate how these reactions are affected by changes in pH and concentrations of the complexing ligands sulfate, SO_4^{2-} and chloride, Cl

Results/Discussion

Mercury(II) was found to sorb strongly to goethite (α -FeOOH), with a gradual decrease in total uptake with increasing pH above 4 (Barrow and Cox, 1992). EXAFS analysis determined that mercury forms bidentate, inner-sphere sorption complexes in a corner-sharing arrangement to the Fe octahedra of the goethite crystal structure (Collins et al., 1999). This sorption mode is unchanged over the pH range examined (4.3 - 7.4). Mercury(II) sorbs much more weakly to γ -alumina (γ -Al₂O₃), but exhibits a substantial increase in total uptake with increasing pH. EXAFS analysis of the sorption products

indicates the formation of a secondary phase at pH 6 which contributes, along with the original substrate, to the removal of mercury(II) from solution. This secondary precipitate was synthesized in the absence of the primary γ -alumina substrate; its EXAFS spectral signature is clearly identifiable as a component of the dual-phase sorption samples initially generated. Formation of such precipitates may be a critical factor in the removal of mercury from aquatic systems, thereby lowering its potential bio-availability and toxicity in the environment. Sorption studies using an amorphous Fe hydroxide precipitate from Knoxville, CA and an amorphous aluminosilicate floc from Sulfur Bank, CA display similar spectral features as the model substrates, suggesting the occurrence of analogous sorption/precipitation processes in natural systems. Mercury(II) sorption to both goethite and γ -alumina is strongly reduced in the presence of chloride due to the formation of aqueous Hg-Cl complexes (Barrow and Cox, 1992). EXAFS analysis of the sorption products shows direct evidence of ternary surface complexes (i.e. Hg-Cl complexes sorbing to the surface) at elevated chloride concentrations. In contrast, mercury(II) sorption is slightly enhanced in the presence of sulfate, likely due to additional ternary surface complex formation. Ligand-variable studies are important in predicting the fate of mercury in natural systems featuring elevated levels of sulfate and chloride, such as regions of hot-spring mercury deposition.

Barrow NJ, Cox VC, *J. Soil. Sci.*, **43**, 295-304, (1992).

Collins CR, Sherman DM, & Ragnarsdottir KV, *J. Coll. Int. Sci.*, **219**, 345-350, (1999).