Mercury Release from Organic Matter (OM) and OM-Coated Mineral Surfaces

University-Led Research

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Mercury released to the environment at the U.S. Department of Energy's Oak Ridge Y-12 Site during the Cold War is now distributed downstream in the floodplain of East Fork Poplar Creek as Hg(II) bound to natural organic matter, mercury sulfide minerals, and methyl-mercury. Strong binding to reduced sulfur in soil or dissolved natural organic matter, organic matter coatings on mineral surfaces, or sulfide minerals may immobilize mercury(II) and/or inhibit methylation reactions. This project is focused on identifying and quantifying binding and release mechanisms of Hg to organic matter, clay minerals, and soils characteristic of the floodplain. We hypothesize that (1) Hg(II) release from reduced sulfur sites requires biogeochemical redox-active agents, whereas release from oxygen sites does not; (2) Mercury bonded to organic matter on clay mineral surfaces is immobilized to a greater extent than Hg(II) adsorbed to uncoated clays; and, (3) Release rates are proportional to the quantity and type of binding site, each of which has a different molecular configuration and therefore different binding strength.

We are investigating adsorption and release of Hg(II) in controlled laboratory experiments using single minerals and natural organic matter. Synopses of sub-projects and results in progress are as follows. (1) Mercury(II) uptake on vermiculite, which comprises 12 to 16% of all minerals in the floodplain soil (N 35°57.959; W 84°21.570), shows an adsorption edge between approximately pH 7.5 and 9.5 in experiments using ~11 mg of solid in 30 mL of an initial 100 ppb Hg(II) solution. Downward shifts of pH by around one pH unit across the edge do not result in mercury(II) release. Work is underway to measure Hg(II) uptake in the presence and absence of well-characterized dissolved organic matter similar to that leached during simulated flooding and drying experiments from floodplain soils (see below). (2) Mercury(II) release from cinnabar under reducing conditions is somewhat higher in the presence of simple quinones, is not pH-dependent over the range of 4.0 to 7.0, and decreases with increasing mass. (3) Using Hg-L_3 edge EXAFS spectroscopy we have characterized the kinetics of mercury(II) binding to dissolved organic matter. (4) To characterize Hg binding to the EFPC soils, we have reassessed how to quantify sulfur speciation in natural organic matter using S-K edge XANES spectra. We refined the Gaussian curve fitting method commonly applied and also used a new linear combination fitting approach to determine sulfur speciation.

We are characterizing mercury release from soil cores collected from the top few tens of cm at a stream bank and floodplain site along the East Fork Poplar Creek downstream from Oak Ridge in simulated flooding and drying experiments (Poulin et al., this volume). Mercury concentration, mercury physiochemical speciation via selective sequential extraction, organic matter content, elemental composition, cation exchange capacity, and soil mineralogy were determined in undisturbed, intact soil cores. Pore fluids during flooding periods were analyzed for total dissolved mercury, elemental indicators of redox state, dissolved sulfate and sulfide, dissolved organic carbon, and colloids. Distinct differences in mercury release kinetics and release mechanisms were observed between O and A horizons. Work is in progress on identifying Hg binding using S-K edge XANES and Hg-L_3 edge EXAFS spectroscopy.