

## Final Technical Report

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

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## Introduction

The goals of the research were to investigate fundamental relationships among mercury, natural organic matter, and selected minerals to better understand specifically the fate and transport of mercury in contaminated soils downstream from the Y-12 plant along East Fork Poplar Creek, Tennessee, and more generally in any contaminated soil. The research conducted at the University of Illinois at Chicago focused on (1) experiments to quantify the uptake and release of mercury from two clay minerals in the soil, kaolinite and vermiculite, in the presence and absence of dissolved organic matter; (2) release of mercury from cinnabar under oxic and anoxic conditions; (3) characterization of the forms of mercury in the soil using synchrotron X-ray absorption spectroscopic techniques; and, (4) determination of molecular forms of mercury in the presence of natural organic matter. We also leveraged funding from the National Science Foundation to (5) evaluate published approaches for determining sulfur speciation in natural organic matter by fitting X-ray Absorption Near Edge Structure (XANES) spectra obtained at the sulfur K-edge and apply optimized fitting schemes to new measurements of sulfur speciation in a suite of dissolved organic matter samples from the International Humic Substances Society. The work so far has resulted in three published manuscripts and four master's theses. Three manuscripts are in preparation from the Master's theses. Two additional manuscripts are in preparation with collaborator Manceau based on spectroscopic results from the field and experiments. (6) A last manuscript with Colorado Ph.D. student Brett Poulin and collaborators Ryan and Aiken will be submitted for publication in September.

### 1. Uptake and Release of Mercury from Kaolinite and Vermiculite

This work resulted in two Master's theses, which are accessible via the University of Illinois at Chicago Indigo website. The results on kaolinite are in the second draft stage of preparation for submission for publication. The results on vermiculite will also be prepared for publication after completion of a few additional experiments.

Heil, Eleanor Melissa (2013) Adsorption of Mercury onto Kaolinite in the Presence and Absence of Dissolved Organic Matter. Master's Thesis, University of Illinois at Chicago, 98 p.

#### Summary:

Adsorption of Hg to kaolinite, a common clay mineral, in the presence and absence of two dissolved organic matter isolates was investigated to assess changes in Hg mobility in soil with increasing defect

density of kaolinite and aromaticity of dissolved organic matter. Batch adsorption experiments were conducted on high and low-defect kaolinite in the presence of high and low aromaticity dissolved organic matter over the pH range 2.9 to 9.5 with varying mercury concentrations. Also, desorption experiments were conducted on high and low-defect kaolinite at pH 7.5-8 with high and low amounts of sorbed mercury in order to examine the effect of time and flooding and drying cycles on the mobility of mercury in soil. In the absence of dissolved organic matter Hg adsorption increased sharply from pH 6 to pH 8 with a slight decrease at pH 9.5 and generally followed the shape of the distribution of mercury hydroxide species. When normalized to total edge surface area the patterns of Hg adsorption onto high and low-defect kaolinite were similar at low mercury concentrations because adsorption dominantly occurred at edge sites. However, with increasing mercury concentration the difference in mercury adsorption, when normalized to total edge surface area, between high and low-defect kaolinite increased, with high-defect kaolinite increasing more, possibly due to the higher abundance of edge sites. The presence of dissolved organic matter increased mercury adsorption at pH < 6 and decreased mercury adsorption at pH > 6. At pH < 6 more mercury was adsorbed in the presence of the more aromatic isolate whereas at pH > 6 more mercury was adsorbed in the presence of the less aromatic isolate. Also, more dissolved organic matter was adsorbed at pH 3 than at pH 8, with the more aromatic isolate adsorbing to a greater extent at both pHs likely because of the preferential adsorption of the aromatic fraction of dissolved organic matter by kaolinite. When normalized to total edge surface area the patterns of Hg adsorption in the presence of dissolved organic matter were similar between high and low-defect kaolinite with the exception of pH > 6 in the presence of the more aromatic isolate. This is likely due to the change in dominant adsorption mechanism of dissolved organic matter from ligand exchange with the edge surfaces of kaolinite at pH < 6 to hydrophobic interactions with the basal surface of kaolinite at pH > 6. Finally, mercury adsorbed to kaolinite was strongly bound and mercury was more strongly bound to high-defect kaolinite than to low-defect kaolinite indicating the key role that kaolinite defect density plays in determining a soils ability to immobilize aqueous mercury.

Kearney, Kenneth E. (2013) Mercury(II) Uptake at the Vermiculite Surface with Relevance to the East Fork Poplar Creek Floodplain. Master's Thesis, University of Illinois at Chicago, 78 p.

#### Summary:

The uptake of mercury(II) onto vermiculite was studied to gain insight into the ultimate fate of this toxic metal in floodplain soils, in particular those of East Fork Poplar Creek, located near Oak Ridge, Tennessee. Batch experiments were conducted at room temperature to determine the effect of pH from 2.1 to 9.5 and the presence of dissolved organic matter at pH 5.3 to 7.3 on mercury(II) uptake. Mercury(II) desorption from vermiculite also was investigated under varying conditions to examine how the natural cycle of wetting and drying may affect the mobility of mercury. In general, mercury(II) uptake onto vermiculite increased with increasing final pH, with a relatively steep increase from 11.5% at pH 8 to 88.5% at pH 9.5. The pH-dependence of the uptake curve is correlated with the distribution of aqueous mercury(II) chloride and mercury(II) hydroxide species. At final pH values from 5.3 to 7.3, the presence of dissolved organic matter did not enhance mercury uptake onto vermiculite. Lastly, mercury adsorbed to the vermiculite structure was strongly bound. A maximum of only 17.5% of the adsorbed mercury(II) was removed under the tested conditions, indicating that vermiculite, and likely other 2:1 phyllosilicates, may immobilize soluble mercury in floodplain environments.

#### 2. Release of Mercury from Cinnabar under Oxic and Anoxic Conditions

This work also resulted in two Master's theses: one (Stallings, 2013) is accessible via the University of Illinois at Chicago Indigo website, and the second (Maley, 2014) will be released for public access by the

summer of 2016. The summaries from each thesis are included below.

Stallings, Kimberly Boyd (2013) Mercury Release from Cinnabar in Water and Aqueous Solutions of Hydroquinone or Ascorbic Acid. Master's Thesis, University of Illinois at Chicago, 76 p.

**Summary:**

The release of mercury from cinnabar in water and aqueous solutions of hydroquinone and ascorbic acid was investigated in batch experiments under various conditions. Experiments were conducted in a nominally anoxic or oxic state using solutions that contained different ratios of reactant to cinnabar and recycled cinnabar; variable mass of cinnabar; and variable pH. Mercury concentrations were obtained using Cold Vapor Atomic Fluorescence Spectroscopy. The amount of mercury released in the presence of hydroquinone was about the same as that released in solutions of water under both anoxic and oxic conditions. In the presence of each of these reactants, more mercury was released than in the presence of ascorbic acid. Decreased release of mercury with increased cinnabar concentration was observed in experiments containing water or water and hydroquinone, which is likely an effect of particle aggregation and the effective decrease of the number of exposed reactive surface sites. Recycled cinnabar surfaces released less mercury than the initial surfaces. The amount of sulfate measured in selected solutions is two to three orders of magnitude greater than the amount of mercury released. Furthermore, pH over the range of ~ 3 to 8 did not measurably affect the release of mercury from cinnabar. Altogether the results indicate a strong dependence of the release of mercury from cinnabar on the presence of oxygen. The oxidation of sulfur species at the surface of cinnabar likely weakens mercury-sulfur bonds releasing mercury to solution; or, oxidized sulfur species may remain at the surface, increase in concentration and eventually slow the reaction. Any available reductants may be able to remove the oxidized layer and promote dissolution.

Maley, Ellen Marcia (2014) Effect of Cinnabar Age on Release of Aqueous and Volatile Mercury. Master's Thesis, University of Illinois at Chicago, 77 p.

**Summary:**

Mercury release from cinnabar ( $\alpha$ -HgS) in aqueous solutions was evaluated as a function of the age of cinnabar after pretreatment. Seventy-three batch experiments were conducted with powdered cinnabar aged from <2 h up to 7.4 y after cleaning in 10% nitric acid to remove fines and suspected surface alteration products. Cinnabar was reacted with water and the amounts of released aqueous and volatile mercury were quantified. Solutions were in equilibrium with either air or nitrogen/argon atmospheres, and some air-equilibrated solutions were also adjusted with sodium chloride and/or nitric acid or sodium hydroxide. Mercury release from cinnabar of a known age was 10 times higher after 30 min than after 1 d, indicating that a pulse of mercury is released initially upon solution/sample contact, and then re-adsorbed to the cinnabar surface. At near-neutral pH, in the presence of oxygen, the amount of total released Hg increased systematically with age to a value 100 times higher at 656 d age ( $1.58 \times 10^{-4}$  mol Hg m<sup>-2</sup> HgS) than at < 0.1 d age ( $1.85 \times 10^{-6}$  mol Hg m<sup>-2</sup> HgS) in 30 min reactions. Released Hg decreased from 656 d to 2453 d age ( $9.89 \times 10^{-6}$  mol Hg m<sup>-2</sup> HgS). Mercury release was enhanced by two times in the absence of oxygen. Mercury(II) was the dominant species released in most experiments and generally followed the same pattern as total Hg with cinnabar age. Mercury(0) peaked at 6 d and decreased systematically with increasing age up to 656 d, and was variable from 2453 to 2709 d aged cinnabar. These observations suggest that changes in surface composition caused the variation in mercury release over time. Mercury release normalized to initial surface area of the cinnabar decreased with increasing mass. This relationship along with observations of hydrophobic aggregation and particle dispersion also indicate that the surface/solution interaction changed with increasing cinnabar age and

may have caused the high variability observed in some replicate experiments. The patterns of released mercury in these experiments imply that cinnabar may not be a permanent sink for mercury in the environment.

### **3. Characterization of the Forms of Mercury in East Fork Poplar Creek Soil using X-ray Absorption Spectroscopy**

The distribution of mercury in intact thin sections of soil from the top 5 cm of the East Fork Poplar Creek floodplain was characterized by micro-X-ray fluorescence mapping, micro-X-ray diffraction, and micro-EXAFS spectroscopy at the Advanced Light Source, Beamline 10.3.2. Results show that the hotspots of mercury are aggregated nanoparticles of metacinnabar and that mercury is also distributed throughout the fine-grained organic matter in the soil in a form that is likely nanoparticulate metacinnabar, but which cannot be identified at this beamline. Metacinnabar was not associated with any particular macromolecular organic matter such as rootlets or woody material, with the exception of one observation where metacinnabar lined an organic particle in the shape of a seed. In contrast, germanium, which has a fluorescence signal close to that of mercury, is ubiquitous in the soil and often lines macromolecular organic material. A manuscript is in preparation on these results.

### **4. Molecular Forms of Mercury in the Presence of Natural Organic Matter**

This research has resulted in two publications thus far. In the first, by Nagy et al. (2011), a new binding environment for mercury in solid natural organic matter (peat) was identified using Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy at liquid helium temperature on samples with added mercury at ~50-60 ppm (mg Hg/kg peat). Measurement at liquid helium temperature allowed the characterization of bond lengths and ligand numbers that are difficult to observe at room temperature because of the chemically 'soft' nature of the mercury-sulfur bonds. The new binding environment was a multinuclear Hg-S structure that resembled metal centers in metallothionein proteins. We also tentatively identified a structure at much higher amounts of added mercury that implicated a role of aromatic structures in the binding mechanism.

In the second publication, by Manceau et al. (2015), high energy-resolution XANES spectroscopy at the Hg L3 edge and liquid helium temperature was used to characterize the proportions of linear organo-sulfur-mercury (RS-Hg-SR) complexes and nanoparticulate metacinnabar in the soil organic matter at the Horizon Site on East Fork Poplar Creek approximately 17 km downstream from the Y-12 National Security Complex and to track the evolution of Hg speciation as mercury reacted with dissolved organic matter for periods of up to six months. The application of high energy-resolution XANES to the mercury system was made for the first time in this study, and the work was conducted at the European Synchrotron Radiation Facility beamline ID-26. The results demonstrate that the technique provides the highest sensitivity yet obtained at any synchrotron to determine the speciation of mercury in complex materials. The results from the experiments showed that the same proportions of the two mercury species were obtained by reacting mercury with dissolved organic matter under abiotic oxic conditions for six months. A molecular mechanism derived from first principles calculations was proposed for the reaction of RS-Hg-SR complexes with each other to form the nanoparticulate metacinnabar. The similarity in proportions of the two mercury species in experiments and the surface soil suggests that at least some of the nanoparticulate metacinnabar in the East Fork Poplar Creek floodplain may have formed abiotically in the presence of oxygen. Free sulfide generated by sulfate-reducing microbes is not necessary for the nucleation of nanoparticulate metacinnabar.

One additional manuscript will be submitted within the coming year. The paper will focus on the results of a set of experiments designed to investigate the interaction of mercury at different concentrations with dissolved organic matter of different origins and having different sulfur speciation for periods of up to one year. The evolution of the forms of mercury is being characterized using high energy-resolution XANES.

Nagy K. L., Manceau A., Gasper, J., Ryan J. N., and Aiken G. R. (2011) Metallothionein-like multinuclear clusters of mercury(II) and sulfur in peat. *Environmental Science & Technology* 45, 7298-7306. DOI: 10.1021/es201025v.

Manceau A., Lemouchi C., Enescu M., Gaillot A.-C., Lanson M., Magnin V., Glatzel P., Poulin B. A., Ryan J. N., Aiken G. R., Gautier-Luneau I., and Nagy K. L. (2015) Formation of mercury sulfide from Hg(II)-thiolate complexes in natural organic matter. *Environmental Science & Technology*, 49, 9787-9796. DOI: 10.1021/acs.est.5b02522.

## **5. Sulfur Oxidation States in Natural Organic Matter using XANES Spectroscopy**

This research was conducted with leveraged funding from the National Science Foundation. The approach described in the publication by Manceau and Nagy (2012) was applied to characterize the dissolved organic matter used in the experiments described in the previous section, and in particular, in the last set of experiments that will be described in the forthcoming journal submission.

Manceau A. and Nagy K. L. (2012) Quantitative analysis of sulfur functional groups in humic substances by XANES spectroscopy. *Geochimica et Cosmochimica Acta* 99, 206-223.

## **6. Characterization of Mercury Release Patterns in O and A Horizon Soils from the East Fork Poplar Creek Floodplain**

The collaboration with Ryan and Aiken has trained one Ph.D. graduate student at the University of Colorado, Brett Poulin, who is lead author on a manuscript to be submitted to *Geochimica et Cosmochimica Acta* imminently. The manuscript content is described in the Final Technical Report of Collaborator Aiken under Award Number DE-SC0001783. Briefly, the results indicate that similar biogeochemical processes control the release of mercury and the forms of released mercury in both batch experiments and intact soil column experiments under simulated flooding conditions. The current working title is “Distinctive mercury transformation and release dynamics along a riparian soil profile under flooding conditions” and the authors are Brett A. Poulin, George R. Aiken, Kathryn L. Nagy, Alain Manceau, David P. Krabbenhoft, and Joseph N. Ryan.