Introduction

This collaborative study was designed to assess the role of organic matter in the fate and transport of mercury from contaminated Oak Ridge soils. The specific charge for the U.S.G.S. portion of the study was to provide analytical support for the larger group effort (Nagy and Ryan), especially with regard to analyses of Hg and dissolved organic matter, and to provide information about the release of mercury from the soils. Progress made during the first year of funding included the selection and characterization of the study site, with emphasis on selecting a study site appropriate for the collection of intact soil cores. During year 2, the USGS lab contributions included (1) the characterization of East Fork Poplar Creek water for chemical properties, (2) performing selective sequential extractions on flood plain soil to determine mercury physiochemical speciation, (3) assistance in the collection of intact soil cores from the study site, (4) pore water analyses of dissolved cations, anion, and alkalinity, (5) characterization of changes in dissolved organic matter (DOM) quality and quantity in pore water samples from saturated Oak Ridge soils, (6) assessment of the influences of Fe on fluorescence properties of porewater DOM, and (7) mercury analyses of soils and water samples. During the final year of funding, we (1) investigated mercury transformation and release dynamics using microcosm experiments, (2) characterized solid phase mercury speciation in Oak Ridge soils using X-ray absorption spectroscopy, and (3) prepared two manuscripts for publication. Microcosm experiments were conducted to further investigate the biogeochemical controls on mercury

release and transformation in Oak Ridge soils under various redox regimes. Microcosm experiments complemented previous work conducted during years 1 and 2 of the project using intact soil cores. X-ray absorption spectroscopy was used to characterize solid phase mercury speciation in Oak Ridge soils and proved valuable in characterizing long-term mercury transformation in this system.

East Fork Poplar Creek Characterization

Surface water samples were collected from East Fork Poplar Creek during base flow in June, 2010 and during high flow in October, 2010. Surface water samples were analyzed for cations, anions, alkalinity, dissolved organic carbon (DOC) concentration, the specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), DOM fluorescence, and both particulate and dissolved mercury and methylmercury (Table 1).

Table 1. General chemical properties of East Fork Poplar Creek surface waters during a low flow and high flow event.

Aqueous Composition	Base Flow Aqueous Concentration (6/16/10)	High Flow Aqueous Concentration (10/25/10)
Cl^- (mM)	0.375	0.346
NO_3^- (mM)	0.266	0.195
SO_4^{2-} (mM)	0.231	0.488
Na^{2+} (mM)	0.465	0.561
K^+ (mM)	0.076	0.094
Mg^{2+} (mM)	0.375	0.933

Ca^{2+} (mM)	1.158	2.212
HCO$_3^-$ (mM)	2416	2276
DOC (mg L^{-1})	2.90	3.50
SUVA$_{254}$ (L mg^{-1} m^{-1})	2.24	n/a
pH	7.48	n/a
Particulate Total Mercury (ng L^{-1})	225.3	2286.1
Particulate Methylmercury (ng L^{-1})	0.21	1.677
Filtered Total Mercury (ng L^{-1})	26.9	22.5
Filtered Methylmercury (ng L^{-1})	0.567	0.276

Selective Sequential Extractions of Flood Plain Soils

Selective sequential extractions were conducted on flood plain soils (0-5 cm, 20-25 cm, and 40-45 cm depth) to identify mercury physiochemical speciation as a function of depth in the soil column. Sequential extractions were previously conducted on stream bank soils (0-5 cm, 20-25 cm, and 40-45 cm) during year 1 funding. Details on the sequential extraction method and mercury physicochemical species distribution determined in stream bank soils can be found in the progress report from funding year 1.

The three soil depths were selected to represent the dominant soil horizons, designating 0-5 cm depth to represent the O horizon, 20-25 cm depth to represent the A horizon, and 40-45 cm depth to represent the B horizon. Sequential extraction data from flood plain soils contrast those from the stream bank site. At the soil surface (0-5 cm), 73% of the mercury is associated with soil organic matter, with only 1.8% of the mercury present in the F5 aqua regia digestions (recalcitrant mercuric sulfide phases). At greater depths in the soil column (20-25 cm, 40-45 cm), mercury is associated less with soil organic matter and more with recalcitrant mercury phases (F4 and F5). Between all three flood plain soils analyzed, the highest distribution of

mercury in the F5 fraction was only 10.7%, contrasting results from stream bank soils were as much as 74% of the total mercury was found in the F5 fraction. In summary, the two study sites contrasts in their total mercury depth profiles and the phases of mercury present. The flood plain site has elevated mercury levels present at the soil surface that quickly dissipates with increased depth, which consist of predominantly mercury-organic matter phases. In contrast, the stream bank site consists of significantly greater mercury concentrations that peak at 20-25 cm depth in the soil column, dominated by recalcitrant mercury phases.

Pore Water Sampling Analyses and Results

Our characterization of pore water from saturated soil cores included DOC concentration, $SUVA_{254}$, DOM fluorescence, cations (Ca^{2+}, Mg^{2+}, K^+, Na^+), anions (Cl^-, NO_3^-, SO_4^{2-}), and alkalinity. Tracking changes in terminal electron acceptors (NO_3^-, SO_4^{2-}), as well as alkalinity and cation concentrations, provides valuable information on the redox status of the soil core. Over the duration of the saturation events both NO_3^- and SO_4^{2-} were reduced to below instrumental detection limits, followed by an increase in total dissolved Fe and Mn. These results demonstrate that the simulated saturation events are producing reducing conditions within the soil core, causing the exhaustion of NO_3^- and SO_4^{2-} and reductive dissolution of Fe and Mn mineral phases. Over this same time period concentrations of HCO_3^- increased linearly, generated from biologic $CO_{s\,(g)}$ production, as did cation concentrations.

In both the O and A soil horizons DOC concentrations increased linearly during saturation events 1 and 2 (Fig. 1 and 2). We did not observe a strong correlation between dissolved mercury and DOC concentrations in either the O or A horizons, suggesting that changes in pore water DOC concentrations are not the sole driver in mercury release from Oak Ridge soils. Alternatively, up to 34% of the dissolved mercury in saturated soils was found to be associated with colloids between 100 – 450 nm in size, and DOM is known to play a role in the formation and transport properties of colloids in previously studied systems. Future work needs to be conducted to identify the properties of pore water colloids in Oak Ridge soils, which may provide insight to the role of DOM in their fate and transport.

When comparing the DOC release dynamics between saturation events 1 and 2, the kinetics of mercury release are quite similar. Changes in the $SUVA_{254}$ of the pore water DOM, being a proxy for DOM aromaticity, were relatively minor over the duration of the saturation events. For example, the $SUVA_{254}$ of DOM from the O horizon changed by less than 0.5 $SUVA_{254}$ units over the duration of the second saturation event ($t = 34.5$ d). It is likely that although DOM is being decomposed by microbes, in-turn generating $CO_{2\,(g)}$, organic matter is simultaneously leaching from the soil into the pore water. Due to continual changes in the DOM pool over the duration of the saturation event, tracking changes in DOM composition becomes increasingly difficult, and confounds our ability to draw direct conclusions on changes in DOM composition.

DOM fluorescence analyses were conducted on select pore water samples. Our use of quantitative fluorescence parameters, including the fluorescence-index (FI) and fluorescence modeling tools like parallel factor analysis (PARAFAC), have been limited due to the presence of constituents (Fe and Al) known to quench, or reduce, the fluorescence intensity of natural fluorophores. We conducted laboratory studies with natural DOM that demonstrate that elevated levels of Fe can induce considerable changes in DOM fluorescence properties and may hinder efforts to utilize quantitative fluorescence parameters. For that reason we explored spectroscopic correction protocols that can be implemented to eliminate the effects of fluorescence quenching agents on DOM fluorescence. One such method is the adjustment of sample pH to induce metal-complex dissociation. Results of this work have recently been published (Poulin et al., 2014, Effects of Iron on Optical Properties of Dissolved Organic Matter, *Environ. Sci. Technol.*, vol 48, 10098-10106).
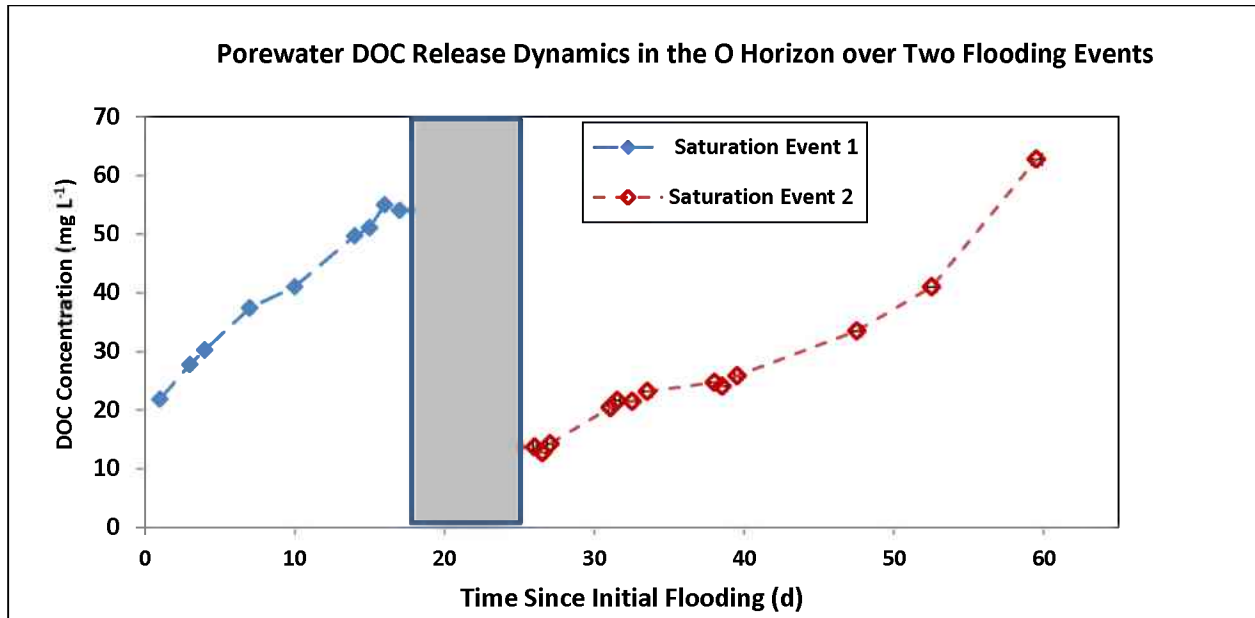
Figure 1. Pore water mercury release dynamics in the O horizon of a stream bank surface core; grey shaded region represents an oxic period between saturation events.
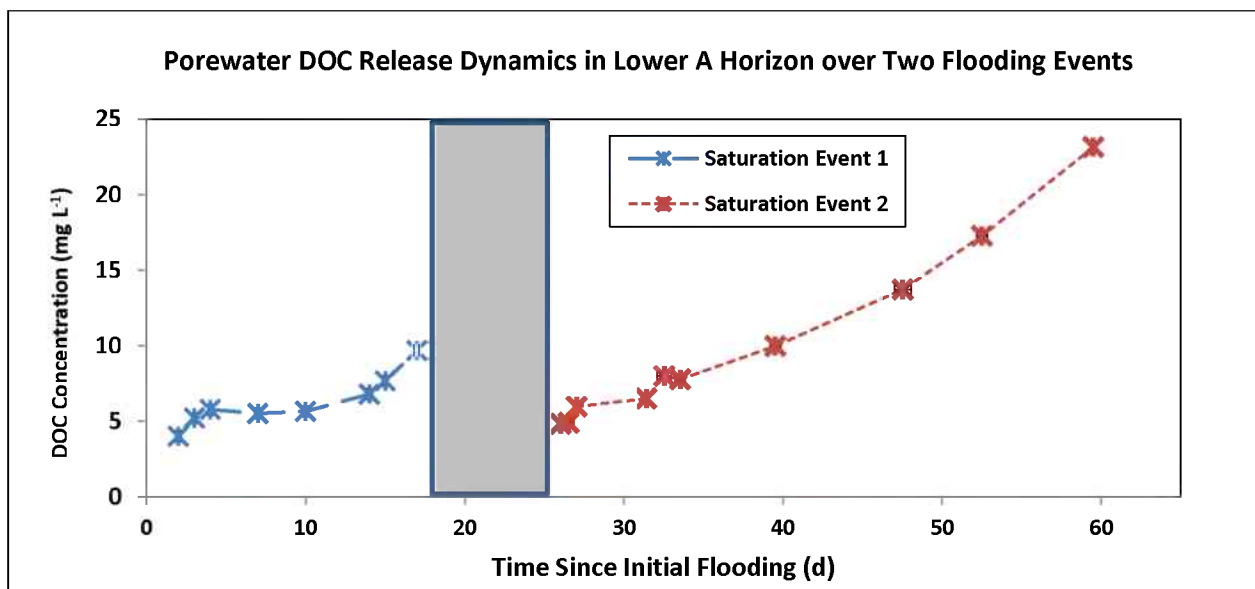

Figure 1. Pore water mercury release dynamics in the Lower A horizon of a stream bank surface core; grey shaded region represents an oxic period between saturation events.

Mercury Transformation and Release Dynamics in Microcosm Systems

Transient redox conditions are known to strongly influence the behavior of mercury in natural environments, but the importance of soil redox status in controlling mercury fate and transport in contaminated riparian soils is not well understood. Our efforts during year 1 and 2 of the project characterized mercury release and transformation in Oak Ridge soils within intact soil cores under saturation conditions. Here we present our finding from similar experiments in microcosms that further characterize the biogeochemical controls on mercury mobilization and transformation.

Mercury release and transformation was investigated in two soil horizons from the East Fork Poplar Creek stream bank under saturation conditions with air-dried O (0-10 cm depth) and A horizon (20-30 cm depth) soils. Soils were previously characterized for total mercury concentration, mercury speciation by selective sequential extraction and X-ray absorption spectroscopy, organic matter content, elemental composition, and soil mineralogy. Individual dark microcosm experiments were performed under a nitrogen atmosphere in duplicate at a 1:1 solid-to-liquid ratio using deionized water. Pore water samples were collected in suction cups (10 μm pore size) at 11 time intervals over 36 days. Unfiltered pore water analyses included pH, E_H, total mercury, methylmercury, dissolved gaseous mercury (e.g., Hg(0)), and major metals (manganese, iron, aluminum). Filtered (0.20 μm) pore water analyses included anions (chloride, nitrate, sulfate, sulfide, acetate, formate), cations (calcium, magnesium), major metals, total mercury, methylmercury, dissolved gaseous mercury, dissolved inorganic carbon, dissolved organic carbon, and dissolved organic matter (DOM) optical properties.

Measurements of E_H dropped immediately following sample inundation, with values reaching a plateau between 10 and 14 day saturation time in both systems. Manganese and iron became present in O horizon pore water after 1 and 5 day saturation, respectively. Manganese and iron release in A horizon soils was slower, becoming present at 5 and 18 days. Sulfate reduction began between 2-3 days following inundation, and sulfate was exhausted in systems at 11 (O horizon) and 13 (A horizon) days saturation. Acetate represented a significant portion of organic carbon in O horizon systems, increasing linearly between 1-18 days, then decreasing to below limits of detection between 18-30 days. The depletion of acetate at late flooding times was attributed to the onset of methanogenisis as indicated by the increase in headspace CH_4 levels. Due to high acetate levels, changes in DOM composition were carried out using the spectral

slope ratio (S_R), as opposed to the more commonly employed specific UV absorbance (SUVA), because values of S_R are largely independent of DOC concentrations.

O-horizon pore waters exhibited a rapid increase in filter-passing and particulate total mercury between 1-2 days following soil inundation. Filter-passing total mercury peaked at 2 days, while particulate total mercury was greatest 3 days after inundation. Filter-passing and particulate total mercury levels decreased to low levels between 3-7 days concurrent with the period of sulfate reduction. No substantial changes in either aqueous mercury pools were observed between 11-36 days. Levels of Hg(0) were relatively low over the entire flooding event and therefore had minor contributions to filter-passing total mercury. Filter-passing methylmercury increased between 1-3 days, remained relatively constant between 3-25 days, and slightly decreased by 36 days. The percentage of filtering-passing total mercury as methylmercury increased from 0.2% at 3 days, to 10.7% at 14 days. Particulate methylmercury showed little variation with flooding time, and accounted from < 0.2% of particulate total Hg. The initial mercury release in O-horizon soils is likely due to the coincident release of DOM of higher molecular weight as evidenced by a decrease in the DOM spectral slope ratio (S_R). The re-association of mercury with O-horizon soils coincided with the period of sulfate reduction and was attributed to direct (e.g., metacinnabar precipitation) and/or indirect scavenging (e.g., mackinawite precipitation and mercury sorption) of mercury by generated sulfide (S(-II)).

In contrast, A-horizon soil pore waters exhibited a significant increase in total mercury at late flooding time (5-18 days) that plateau between 18-36 days. Release behavior of particulate total mercury largely mimicked those of filter-passing total mercury. High concentrations of Hg(0) were observed at late flooding durations that closely matched those of filter-passing total mercury. This indicated that the predominant aqueous mercury phase at late saturation times in A-horizon pore waters was Hg(0). Concentrations of both filter-passing and particulate methylmercury exhibit similar trends to those for total mercury, with low levels at short flooding times and elevated concentrations at late time intervals. Mercury release behavior in A- horizon soils under strongly reducing conditions indicates a release mechanism coupled to redox-sensitive processes. This hypothesis was supported by a positive correlation ($R^2 = 0.79$, $n = 22$) between porewater manganese concentrations, attributed to reductive dissolution processes, and filter-passing total mercury. Flooding experiments with intact soil cores showed similar mercury

release behavior in both the O- and A- horizon soils, which indicates that the same processes control mercury release and transformation in intact, undisturbed soil matrices.

Characterization of Solid Phase Mercury Speciation by X-ray Absorption Spectroscopy

Mercury speciation in O- (0-5 cm depth) and A- horizon (20-30 cm) Oak Ridge soils were characterized by X-ray absorption spectroscopy. We aided in the preparation of fractions of soils required to obtain sufficient solid-phase mercury concentration for spectroscopic analysis. Soil samples were air-dried and sieved to < 2 mm using a stainless steel sieve to remove large rocks and organic debris. The total mercury content of bulk O- and A- horizon soils were 14.8 and 54.9 mg kg^{-1}, respectively, as determined by thermal desorption and atomic absorption spectroscopy detection (Milestone, DMA-80 Direct Mercury Analyzer). The organic matter content of bulk O- and A- horizon soils were 79.6 and 38.8 g kg^{-1}, respectively, as determined by loss on ignition (LOI) at 550° C for 2 h.

O-horizon soil was separated into the clay-size fraction (0.1 μm < X < 2 μm) using sedimentation followed by filtration. 0.5 g soil was added to 40 mL Teflon® tubes containing 40 mL Milli-Q water (>18MΩ cm resistance) for 6 h, sonicated for 2 min to disaggregate minerals, and centrifuged at 1000 rpms for 2 min, removing soil particles > 2 μm assuming a density of 2.65 g cm^{-3}. The suspended clay-size fraction was collected on a 0.1 μm filter (Supor®, Pall Life Science), rinsed with 10 mL Milli-Q water, gently removed from the wet filter, and dried under N$_2$. A- horizon soil were separated into the silt- (2-63 μm) and clay-size fractions (< 2 μm) using a combination of mechanical sieving and sedimentation. First, A-horizon soil was soaked in Milli-Q water for 6 h, sonicated for 2 min to disaggregate minerals, and sieved using a 63 μm stainless steel sieve. Next, the clay-size fraction (< 2 μm) was separated from the silt-size fraction (2-63 μm) by sedimentation. The solution containing < 63 μm soil was sonicated for 2 min, placed in 40 mL Teflon® tubes, and centrifuged at 1000 rpms for 2 min, removing soil particles > 2 μm assuming a density of 2.65 g cm^{-3}. The silt- (2-63 μm) and clay-size (< 2 μm) fractions were dried under air.

The total mercury content was determined on soil fractions by aqua regia digestion (3:1 concentrated trace-metal grade HCl:HNO$_3$; Fisher Scientific), preservation with 1% v/v 0.2 M BrCl, and aqueous analysis using SnCl$_2$ reduction, dual amalgamation, and cold vapor atomic

fluorescence spectroscopy (CVAFS) detection following EPA method 1631 (Tekran 2600; method detection limit of 2.5 pM; relative percent deviation between duplicate analyses averaged 0.7%). A-horizon samples were analyzed in digestion duplicate. The O- horizon sample was analyzed in digestion singlet due to limited sample mass. The total mercury content of O-horizon clay-size fraction was 47.6 mg kg^{-1}. The total mercury content of A-horizon clay- and silt-size fractions were 191 ± 1.8 mg kg^{-1} and 80.7 ± 1.6 mg kg^{-1}, respectively. Soil samples were shipped to Kathryn Nagy and Alain Manceau for spectroscopic analysis.

Collaboration and Dissemination of Results

Results from this study were presented at the 2010 annual meeting of the American Geophysical Union (Poulin and Aiken, 2010, The Effect of Ferric and Ferrous Iron on the Optical Properties of Dissolved Organic Matter. Book of Abstracts, Fall Meeting of the American Geophysical Union December, 2010, San Francisco, CA), the 10th International Conference on Mercury as a Global Pollutant held in Halifax, Canada (Poulin et al, 2011, "Dynamics of mercury release in flooded soils from Oak Ridge, Tenn.", Book of Abstracts 10th International Conference on Mercury as a Global Pollutant, Halifax, Canada), and at the 11th International Conference on Mercury as a Global Pollutant held in Edinburgh, Scotland (Poulin et al., 2013 "Mercury transformation and release dynamics under saturation conditions in contaminated riparian soils" Book of Abstracts, 11th International Conference on Mercury as a Global Pollutant, Edinburgh, Scotland).

Results of this research are in various stages of being published as journal articles. First, a manuscript describing the effects of iron on dissolved organic matter optical measurements has recently been published in Environmental Science and Technology (Poulin et al., 2014, Effects of Iron on Optical Properties of Dissolved Organic Matter, *Environ. Sci. Technol.*, vol 48, 10098-10106). Second, a manuscript entitled "Mercury sulfide forms abiotically from Hg(II)-thiolate complexes in natural organic matter" authored by Alain Manceau, Cyprien Lemouchi, Mironel Enescu, Anne-Claire Gaillot, Martine Lanson, Valérie Magnin, Pieter Glatzel, Brett A. Poulin, Joseph N. Ryan, George R. Aiken, Isabelle Gautier-Luneau, and Kathryn L. Nagy is presently under review. Finally, a third paper entitled "Mercury transformation and release dynamics under

saturation conditions in contaminated riparian soils" authored by Brett A. Poulin, George R. Aiken, Joseph N. Ryan, Alain Manceau, and Kathryn L. Nagy is in preparation for submission to *Geochimica et Cosmochimica Acta.*

Laboratory support from the U.S. Geological Survey included (1) access to an anaerobic glove box for batch experiments, (2) aqueous analyses of dissolved organic carbon concentration (OI-700 total organic carbon analyzer) (3) DOM optical characterization (Agilent 8453 UV-vis spectrophotometer; Jobin Yvon Horiba Fluoromax 3 fluorometer), (4) total solid mercury analyses (Milestone DMA-80 Direct Mercury Analyzer), and (5) total liquid mercury analyses (Tekran 2600).