

Final Project Report

DOE award number: DE-SC0005351

Recipient: University of Illinois

Project Title: “Exploratory Research: Mercury Stable Isotopes as Indicators of the Biogeochemical Cycling of Mercury”

Principal Investigator: Prof. Thomas M. Johnson

Unfunded ORNL collaborators: George Southworth (retired) and Dr. Carrie Miller

Graduate Students Trained: One (Gideon Bartov); no post-doctoral researchers

Executive Summary:

This exploratory project investigated the use of mercury (Hg) stable isotope measurements as a new approach to study how Hg moves and changes its chemical form in environmental systems, with particular focus on the East Fork of Poplar Creek (EFPC) near the DOE Y-12 plant (a Hg contamination source). This study developed analytical methods and collected pilot data that have set the stage for more detailed studies and have begun to provide insights into Hg movement and chemical changes. Almost all of the proposed tasks of the study were completed in the two-year period (including a one-year no-cost extension).

The overall Hg stable isotope approach was effective. The Hg isotope analysis methods yielded high-precision measurements of the sediment, water, and fish samples analyzed; quality control measures demonstrated the precision. The pilot data show that the $^{202}\text{Hg}/^{198}\text{Hg}$, $^{199}\text{Hg}/^{198}\text{Hg}$, and $^{201}\text{Hg}/^{198}\text{Hg}$ isotope ratios vary in this system. $^{202}\text{Hg}/^{198}\text{Hg}$ ratios of the Hg released from the Y-12 plant are relatively high, and those of the regional Hg background in soils and river sediments are significantly lower. Unfortunately, $^{202}\text{Hg}/^{198}\text{Hg}$ differences that might have been useful to distinguish early Hg releases from later releases were not observed. However, $^{202}\text{Hg}/^{198}\text{Hg}$ ratios in sediments do provide insights into chemical transformations that may occur as Hg moves through the system. Furthermore, $^{199}\text{Hg}/^{198}\text{Hg}$ and $^{201}\text{Hg}/^{198}\text{Hg}$ ratio analyses of fish tissues indicate that the effects of sunlight-driven chemical reactions on the Hg that eventually ends up in EFPC fish are measurable, but small.

These results provide a starting point for a more detailed study (already begun at Univ. of Michigan) that will continue Hg isotope ratio work aimed at improving understanding of how Hg moves, changes chemically, and does or does not take on more highly toxic forms in the Oak Ridge area. This work also benefits efforts to trace Hg contamination in the Clinch and Tennessee Rivers, into which EFPC flows, and to distinguish Hg from the Y-12 plant from that released from a nearby coal ash accident.

Comparison of accomplishments with objectives:

The objectives of the project are listed here, followed by accomplishments related to each one:

1. Collection of Pilot Data on stream sediments: Do different potential Hg inputs have differing isotopic “signatures?”

Completed: The pilot data set of 13 analyses (most done in triplicate) is complete and significant differences were observed.

2. Feasibility study: Hg isotope ratio measurements on dissolved/suspended inorganic Hg.

Completed: A fast and efficient preconcentration technique was developed and tested.

3. Pilot Data: Hg isotopes of inorganic Hg in creek water.

Completed: A small pilot data set was collected and provides evidence for the occurrence of certain chemical reactions in the system.

4. Feasibility: Isotope ratios of methyl-Hg.

Completed: A method has been identified that should be effective, but more detailed study revealed a potential problem that must be investigated. This sets the stage for further testing of this method on a variety of water matrices.

5. Pilot Data: Hg isotopes in biota.

Completed: A pilot data set of 8 analyses was generated and suggests minor amounts of photochemical reactions affect Hg in EFPC.

6. Stable isotope spiking as a means of tracing Hg added to laboratory experiments.

Not pursued: This method was discussed with ORNL researchers early in the project. It was decided this method would not be pursued as it was not a high-priority activity for ORNL experiments planned at that time.

Summary of Project Activities

Mercury (Hg) is a highly toxic contaminant with complex biogeochemical cycling. This complexity hinders efforts to predict the environmental impact of Hg and to design effective stewardship strategies for contaminated systems. Improved scientific understanding of the processes involved and the operation of those processes in contaminated sites is needed to improve remediation efforts and long-term stewardship at DOE sites. The general goal of this project was to begin applying a promising new geochemical tool, Hg stable isotope analysis, to enhance understanding of Hg movement and biogeochemical transformation in a creek impacted by large Hg releases from the Y-12 weapons plant near Oak Ridge, TN. Hg stable isotope studies have unique potential to distinguish different sources of Hg, to detect and quantify certain biogeochemical reactions, such as breakdown of methyl mercury and Hg reduction, and to reveal mechanisms of those reactions. This was an exploratory project that addressed feasibility issues and generated pilot data to identify promising areas for further research.

The project was designed around several objectives, posed as scientific questions, and project activities were built around answering these questions. Here, the questions are listed, in italics, with the corresponding project activities and outcomes described.

1. *In the East Fork Poplar Creek site, do different potential Hg source materials (contaminated soils and sediments) formed at different times have differing Hg isotope ratios that can serve as tracers of Hg from various eras? Are they generally distinguishable from those of natural background Hg? If so, will Hg isotope data improve long-term monitoring of Hg sources and migration in the system?*

Methods for measurement of Hg isotope ratios in digested sediments were established in the Illinois laboratory prior to the inception of this project, but because the method was still relatively new, careful quality control measures were carried out to examine the reproducibility of the measurements. Most samples were measured in triplicate. The resulting precise measurements of 12 sediment samples from EFPC provide a first look at Hg stable isotope variations in the system.

The results show that the Hg released from the Y-12 plant has significantly greater $^{202}\text{Hg}/^{198}\text{Hg}$ isotope ratios compared to background Hg found in other streams and rivers of the area (Fig. 1). This shows in sediments near to the current Hg source and in an older layer of sediment that was highly contaminated decades ago. The data do not show any significant difference between old Hg and more recently released Hg, leaving us with an unfortunate lack of ability to distinguish remobilized, older Hg from more recent releases. However, the data do show a general trend toward lower $^{202}\text{Hg}/^{198}\text{Hg}$ ratios in most of the samples found further downstream. Mixing of increasingly dilute Y-12 Hg with background Hg could be responsible for some of this trend, but preliminary mixing calculations suggest mixing cannot explain all of it. Biogeochemical cycling of Hg is the likely cause, with oxidation and mobilization of metallic Hg being a leading candidate process at present. This provided part of the inspiration for a new Hg isotope study led by Rutgers Univ. researchers, and funded by the SBR program, to investigate Hg isotope effects induced by Hg oxidation.

Overall, $^{202}\text{Hg}/^{198}\text{Hg}$ ratios in sediments of EFPC, and other surface water systems around the world, can be used to trace Hg from different sources. They may also provide

evidence for certain biogeochemical processes in EFPC, but further work is needed to define in detail the characteristics of various sources. Anomalous shifts in the $^{199}\text{Hg}/^{198}\text{Hg}$ and $^{201}\text{Hg}/^{198}\text{Hg}$ ratios, which would indicate the influence of photochemical reactions, did not occur in the analyzed sediments, as expected.

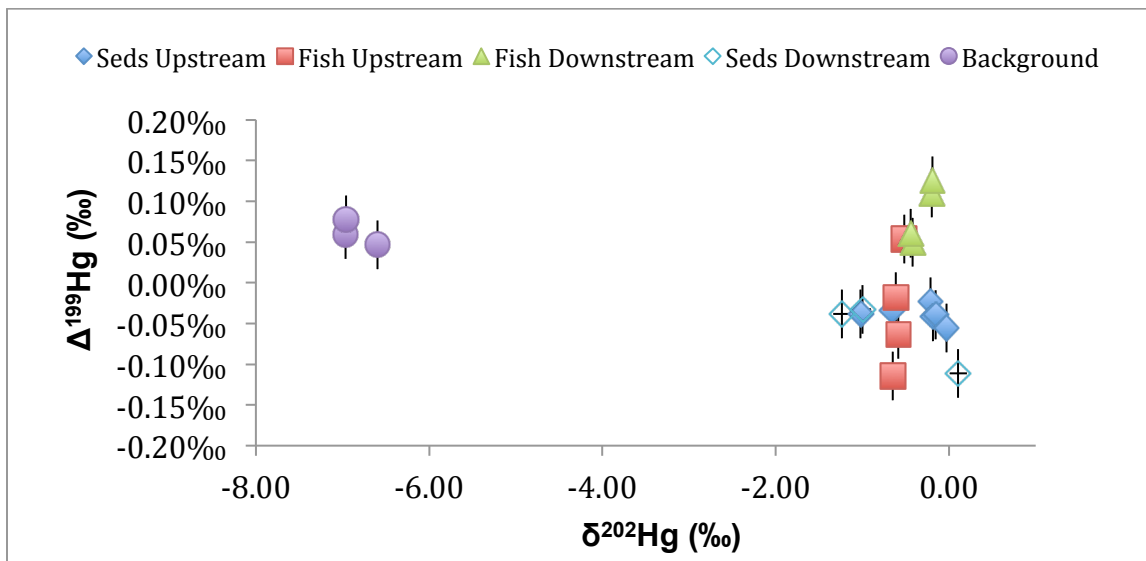


Fig. 1. Analytical data. Sediments impacted by Y-12 Hg have greater $^{202}\text{Hg}/^{198}\text{Hg}$ ratios (expressed here as delta; parts per thousand deviation from NIST SRM-3133) than background samples. Most downstream sediment samples are shifted to lower values from the near-zero values close to the Y-12 plant. Fish tissues show significant $^{199}\text{Hg}/^{198}\text{Hg}$ anomalies, indicating photochemical reactions have affected the Hg prior to its uptake by the fish.

- *Can inorganic Hg be readily preconcentrated from creek waters at the site to enable high-precision Hg stable isotope analyses, and if so, are there variations that suggest a more detailed study will enhance ORNL-SFA efforts (e.g., through detection of Hg reduction)?*

The preconcentration methods developed in this project were effective for EFPC waters. Following published methods, inorganic Hg was efficiently collected onto ion exchange resin from large volumes of water, up to one liter. Interference from dissolved organic compounds was a concern, but was found to be minimal. Recovery of the Hg from the resin was accomplished via a thiourea solution. Initially, this solution proved to be detrimental to the following mass spectrometry steps, but this was remedied via addition of sodium hydroxide.

Variations were detected, but because the sample preparation and analysis is quite time-consuming, only four samples were analyzed. The variations observed suggest more detailed sampling and analysis will reveal information about certain biogeochemical processes in the creek, such as photochemical Hg reduction.

- *Can methods for methyl mercury preconcentration can be developed to enable high precision Hg stable isotope measurements on site waters and if so, will future efforts to develop and make the measurements improve determination of methyl mercury breakdown rates and mechanisms?*

As described in the proposal for this project, collecting sufficient methyl mercury (MeHg) for isotope ratio measurements is a daunting challenge because the MeHg concentrations are extremely low and roughly ten to thirty liters of water must be processed. An existing method for preconcentrating MeHg using a combination of thiol resin and

thiourea [Shade, C.W., and Hudson, R.J.M., Environ. Sci. Technol. 39: 4974-4982 (2005)] was examined. This method works well for measurements of MeHg concentration, but for isotope measurements it would need to be scaled up to by a factor of about one hundred, requiring a much larger system and very long collection times. An important difficulty was identified: The long exposure of the thiol resin to dissolved oxygen, organics, and various other species may destroy or deactivate the thiol groups on the resin. The next step is to build a scaled-up version of the apparatus and determine if this potential problem can be overcome. Other groups are working on more standard ethylation methods to accomplish the same task. These may be more easily scaled up, and it would be wise to follow their progress before moving forward with the thiol resin approach.

- *Can Hg stable isotope analyses of biota serve as proxies for direct measurements of methyl mercury and if so, are there variations that suggest a more detailed study will enhance the overall ORNL-SFA effort?*

Fish tissue samples obtained from ORNL archives were analyzed using methods similar to those used for sediment digestion and analysis. Again, samples were analyzed in triplicate and other quality control measures were undertaken to ensure high-precision data were obtained. The results reveal significant departures of $^{199}\text{Hg}/^{198}\text{Hg}$ and $^{201}\text{Hg}/^{198}\text{Hg}$ ratios from those that would be expected from the $^{202}\text{Hg}/^{198}\text{Hg}$ results.

These shifts in the odd isotope abundances can be attributed to photochemical reactions that affected the Hg prior to its uptake by the fish. The shifts are rather small, indicating these reactions are not greatly impacting the Hg that eventually ends up in EFPC fish. Although these results do not prove that fish analyses record Hg isotopes ratios of the MeHg in the creek water, other researchers have presented evidence this is the case. It appears that Hg isotope analyses of biota should be useful in revealing biogeochemical processes in EFPC.

Relationship with a closely related project: As this project was beginning, the Illinois group also became involved with a project using Hg isotope ratios to trace Hg released from a large coal ash spill in Kingston, TN, on the Clinch River a few miles downstream from the location where EFPC enters the river. The sediment data from this project helped to distinguish Hg sourced from the Y-12 complex from that related to the coal ash spill. The no-cost extension was taken on this project so that a single graduate student could pursue both projects simultaneously.

Dissemination of Results: Results have been discussed with University of Michigan researchers who have obtained funding from the SBR program to continue the study of Hg isotopes in the EFPC system. Results were also discussed with ORNL researchers working Hg contamination at EFPC, at the annual SBR principal investigators meetings in 2011 and 2012.

Journal article in preparation: "Hg Isotope Ratios as indicators of Hg sources and biogeochemical transformations in a contaminated creek system." Planned submission to Environmental Science and Technology in fall, 2012.