

Isotopic Characterization of Mercury in the South River, Virginia
Briefing Paper
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Prepared for the South River Science Team Remediation Options Program October Meeting by
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1. Introduction

The measurement of mercury (Hg) isotope ratios in environmental reservoirs has been used in recent studies to identify sources of anthropogenic Hg and trace the movement of Hg between and within reservoirs. High precision measurements of Hg isotopic composition are made possible by separation and concentration of Hg from samples followed by introduction of a cold Hg vapor into the plasma source of a multi-collector inductively coupled mass spectrometer (MC-ICP-MS). Hg has seven stable isotopes (with masses 196, 198, 199, 200, 201, 202, and 204) and participates in a variety of redox reactions, which can cause isotope fractionation. Hg can undergo two general types of isotope fractionation: mass-dependent fractionation (MDF) and mass-independent fractionation (MIF). MDF occurs in reactions with nuclear mass selectivity, and is generally reported as the $\delta^{202}\text{Hg}$ value¹, where:

$$\delta^{202}\text{Hg} (\text{‰}) = \left(\left[\frac{(^{202}\text{Hg}/^{198}\text{Hg})_{\text{Sample}}}{(^{202}\text{Hg}/^{198}\text{Hg})_{\text{NIST3133}}} \right] - 1 \right) \times 1000$$

MDF has been observed in a number of biological reactions, including microbial methylation and reduction. MIF occurs in reactions with nuclear spin selectivity, and is reported as $\Delta^{199}\text{Hg}$ or $\Delta^{201}\text{Hg}$, calculated as the deviation of the odd-mass isotopes from the predicted kinetic isotope fractionation law in units of ‰. For Hg, MIF has mostly been observed as the result of photochemical reactions^{2,3}.

2. Proposed Work

The objective of this project is to utilize variations in natural Hg stable isotope composition to enhance understanding of Hg sources, mobility, speciation and bioavailability in the South River. An emphasis will be placed on providing new constraints on the chemical and biological processes that lead to methylmercury (MeHg) production, degradation, transport and uptake by aquatic organisms. The Hg stable isotope method has proven useful at other similar sites such the area near Oak Ridge Tennessee⁴, and there is great potential for adding new insight to the factors and mechanisms leading to methylation, transport and biological uptake of Hg in the contaminated South River ecosystem and other nearby stream ecosystems. Specific objectives of the proposed work include:

1. Characterize the spatial variability of the Hg isotopic composition in channel, bank and overbank sediments in a longitudinal transect of the South River from 1 mile upstream of the DuPont facility to 20 miles downstream and in several reference sites.
2. Characterize the Hg isotopic composition of the plant outfall and potential point sources of mercury downstream of the DuPont site to the South Fork of the Shenandoah River.

3. Characterize the Hg isotopic composition of creek bottom periphyton, select benthic organisms, and several fish species such as stoneroller minnows (*Campostoma anomalum*), redbreast sunfish (*Lepomis auritus*) and smallmouth bass (*Micropterus dolomieu*) from sites in South River within the first ten miles after the outfall to obtain the isotopic signature of IHg and MeHg in the creek at various sites.
4. Evaluate the concentration of chemically labile Hg in sediment using dilute acid extraction and measure the Hg isotopic composition of this more biologically available pool to determine whether it is the same or different from Hg in bulk sediment.
5. Characterize the Hg isotopic composition of filtered stream water, suspended sediment and stream bank piezometer water to explore interconnections of flood plain pore groundwater with streamwater.

3. Field Sampling

An initial field sampling campaign to acquire samples for isotope analysis was conducted by Rich Landis and Scott Gregory on April 9th and 10th, 2014. During this initial sampling, sediment and bank soil samples were collected from the following locations within the South River: SR-01 reference site, Outfall-011, Relative River Mile (RRM) 0.25 (Constitution Park), RRM 1.7, RRM 3.5, RRM 8.5, RRM 11.8, RRM 22.1, and floodplain site Wertman Pond. Sediment and bank soil samples were shipped frozen to the BEIGL lab at The University of Michigan.

A second field sampling campaign to collect filtered stream water, suspended sediment and stream bank piezometer samples was conducted between June 24th and 26th, 2014 and involved three members of the Blum lab group and Rich Landis. Filtered water and suspended sediment samples were collected at each of the locations where sediment and bank soil had been collected during the initial field sampling effort, as well as at reference sites on the Middle River (MR-01) and the South Fork Shenandoah (SFR-01). The stream bank piezometers at the RRM 3.5 site were sampled for filtered water and suspended sediment using a portable peristaltic pump. Water samples were collected, filtered, and preserved in the field, using trace-metal clean sampling methods involving a hand operated vacuum-pump and disposable, pre-cleaned 45µm filter housings. Filters and water samples were placed in refrigerated storage at the end of each sampling day, and transported in coolers back to the University of Michigan.

4. Laboratory Status

As of the time of writing, all of the sediment and bank soil samples collected during the April field sampling effort have been analyzed. The filters collected during the June sampling trip, representing the suspended mercury load, have been processed for analysis and combusted. Surface water samples collected in June have not yet been processed, but we plan to begin the processing this fall.

5. Results

The THg concentrations of the sediment and bank soils collected along the longitudinal transect of the South River are presented in Figure 1 (see Appendix 1). The concentration

profiles are in general agreement with previous studies. The bank soil THg concentrations peak at 65ppm directly downstream of Outfall 011, while the sediment concentrations peak at 45ppm around RRM 3.5, with concentrations decreasing dramatically farther downstream.

The longitudinal variation in $\delta^{202}\text{Hg}$ values in the South River is shown in Figure 2. The $\delta^{202}\text{Hg}$ values for the upstream reference site SR-01, presumed to be representative of the regional background $\delta^{202}\text{Hg}$ values, are -1.01‰ for the bank soil and -1.27‰ for the sediment. This is isotopically distinct from the first contamination impacted site, Outfall 011, where the bank soil and sediment $\delta^{202}\text{Hg}$ values are -0.65‰ and -0.60‰ respectively. Within the initial reach below Outfall 011, sediment and bank soil samples have very similar $\delta^{202}\text{Hg}$ values, indicating that the mercury came from the same source and has not been modified by fractionation. Wertman Pond samples (floodplain pond) appear to be isotopically similar to mercury in sediment directly upstream, in line with the hypothesis that movement of sediment loads during flood events is a source of mercury to floodplains. At site RRM 22.1, $\delta^{202}\text{Hg}$ values trend toward a mixture between regional background and contaminated source signals.

The longitudinal change in the $\Delta^{199}\text{Hg}$ values of the bank soils and sediments along the longitudinal transect is depicted in Figure 3. As with the $\delta^{202}\text{Hg}$ data, we observe a significant difference between the regional background values at SR-01 (-0.21‰ for sediment and -0.18‰ for bank soil) and the contamination impacted sites (0.04‰ for sediment and 0.03‰ for bank soil). At sites farther downstream, the increased $\Delta^{199}\text{Hg}$ values may be evidence of photochemical reduction and subsequent loss of $\text{Hg}(0)$ from bank soils.

Through a comparison of MDF and MIF, represented by $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$, we can explore interactions between various Hg reservoirs. The sediment and bank soil data are plotted as $\delta^{202}\text{Hg}$ vs. $\Delta^{199}\text{Hg}$ in Figure 4. The sediment data falls into two groupings, representing the influence of the regional background Hg isotopic value and the contaminated source value. The two distinct groupings suggest that the Hg in the sediments in the South River follows a simple two end-member mixing model. The sediment samples do not appear to be influenced by a third isotopic end-member, such as the atmospheric end-member that was observed to influence the sediments in the contaminated East Fork Poplar Creek near Oak Ridge, TN⁴. Several of the bank soil samples do not appear to fit a simple two end-member mixing model. This suggests either an additional Hg source or isotopic fractionation due to changes in Hg speciation, but more research is necessary to determine what processes may be influencing the bank soils.

6. Preliminary Conclusions

Some of the preliminary conclusions we can draw from the sediment and bank soil data are presented below. We expect to fill in many of the gaps in our understanding of the system with mercury isotope analyses of the suspended and dissolved Hg loads of the South River system. An important conclusion we can draw from the initial sediment and bank soil samples is that the regional background mercury source is isotopically distinct in both $\Delta^{199}\text{Hg}$ and $\delta^{202}\text{Hg}$ from the mercury derived from the source of contaminated media. The difference between source and regional background isotopic signatures is significantly large to allow for determination of the source for various pools of mercury within the South River fluvial system. The mercury load in the streambed sediments of the South River follow a two end-member mixing model, unlike a previously studied contaminated fluvial system at Oak Ridge, TN⁴. We also observed that within the initial reach below Outfall 011, sediment and bank soil samples have very similar $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values, suggesting the mercury came from the same source and has not been modified by

fractionation. Further downstream sediment and bank soil samples deviate in $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values suggesting different sources or fractionation processes. Finally, there is preliminary evidence from the $\Delta^{199}\text{Hg}$ data that photochemical reduction and loss of $\text{Hg}(0)$ is occurring within the South River at downstream locations, although further work needs to be done to better understand the role of photochemical reactions within the system.

References

1. Blum, Joel D, and Bridget a Bergquist. 2007. "Reporting of Variations in the Natural Isotopic Composition of Mercury." *Analytical and Bioanalytical Chemistry* 388 (2) (May): 353–9.
2. Blum, Joel D., Laura S. Sherman, and Marcus W. Johnson. 2012. "Mercury Isotopes in Earth and Environmental Sciences." *Annual Review of Earth and Planetary Sciences* 42 (1)
3. Bergquist, Bridget A, and Joel D Blum. 2007. "Mass-Dependent and -Independent Fractionation of Hg Isotopes by Photoreduction in Aquatic Systems." *Science*. 318 (5849) (Oct): 417-420
4. Donovan, Patrick M, Joel D Blum, Jason D Demers, Baohua Gu, Scott C Brooks, and John Peryam. 2014. "Identification of Multiple Mercury Sources to Stream Sediments Near Oak Ridge, TN, USA." *Environ. Sci. Technol.*, 48 (7), pp 3666–3674

Appendix 1: Figures

Figure 1- THg Concentration Along Longitudinal Transect of South River

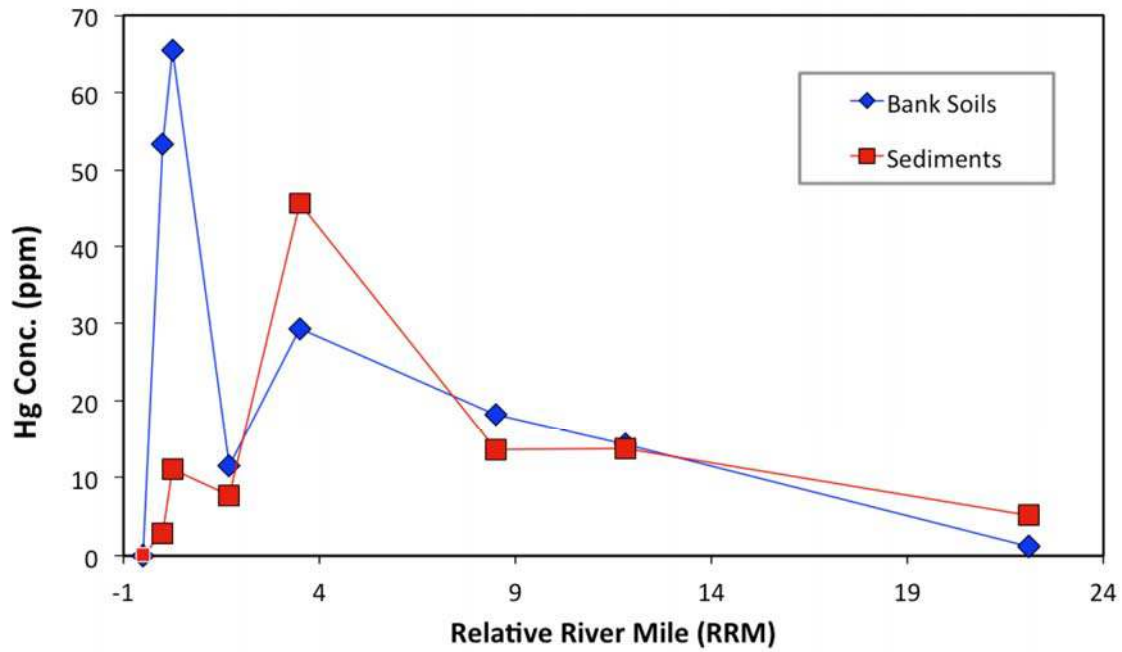


Figure 2 - $\delta^{202}\text{Hg}$ Values Along a Longitudinal Transect of the South River

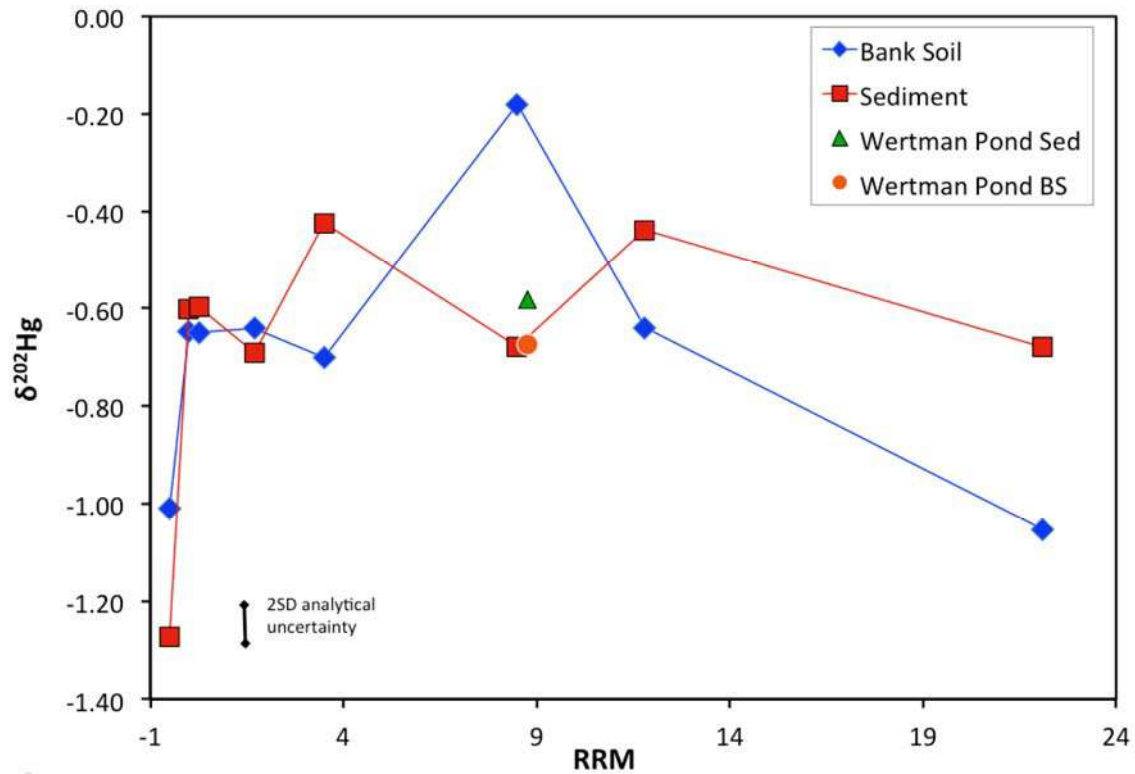


Figure 3 - $\Delta^{199}\text{Hg}$ Values Along a Longitudinal Transect of the South River

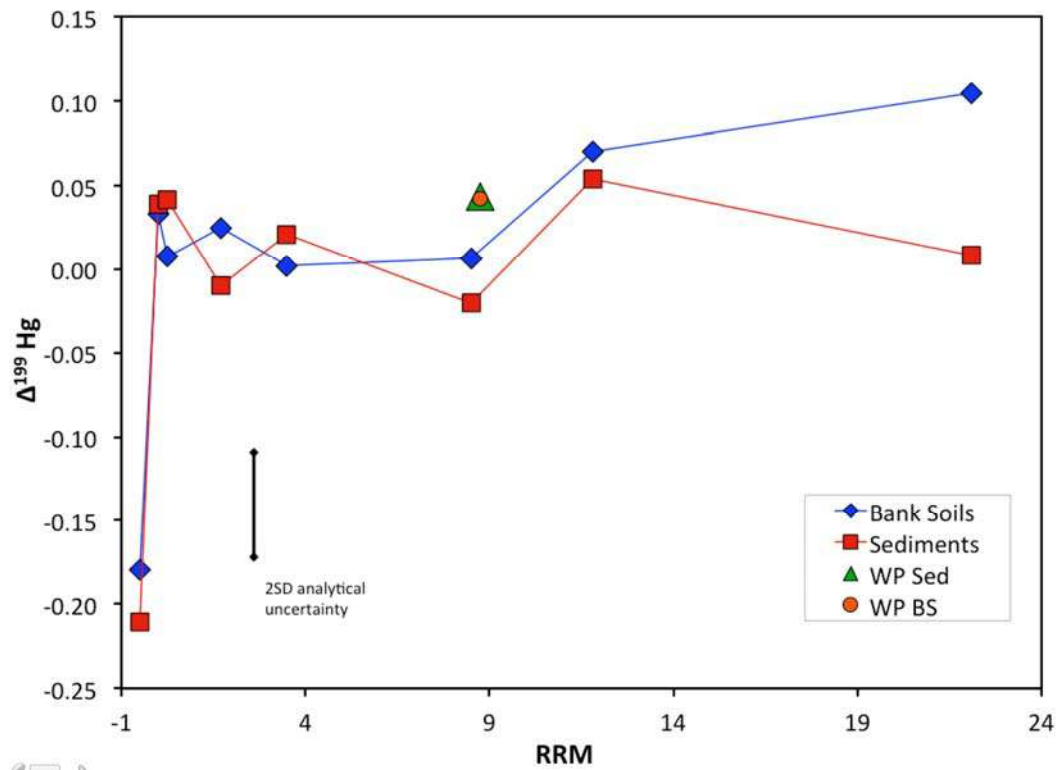


Figure 4 - Plot of $\Delta^{199}\text{Hg}$ (MIF) vs. $\delta^{202}\text{Hg}$ (MDF)

