

Isotopic Characterization of Mercury in the South River, Virginia
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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 reservoirs. High precision measurements of Hg isotopic composition are made possible by separation and concentration of Hg from samples followed by introduction as a Hg cold 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 permil (‰). For Hg, MIF has mostly been observed as the result of photochemical reactions^{2,3}.

2. Field Sampling

An initial field sampling campaign to acquire samples for isotope analysis was conducted by DuPont personnel 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 Blum 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 DuPont personnel. 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 and using 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.

During June of 2015, as a follow-up investigation DuPont personnel collected additional filtered water samples from the on-site wastewater treatment site Outfall 001 to allow characterization of the isotopic signature of this potential Hg source. These water samples were shipped back to the University of Michigan for analysis.

3. Laboratory Status

All of the sediment and bank soil samples collected during the April 2014 field sampling effort have been analyzed. Additionally, all of the filters and associated filtered surface water collected during the June 2014 field sampling effort have also been analyzed. The filtered surface water from the upstream reference site SR-01 and the filtered surface water from the MR-01 reference site have been analyzed for THg concentrations, but values in these samples were too low to obtain accurate isotope data. The filtered surface water from Outfall 001 collected during June of 2015 has been analyzed for THg, and is currently being processed for isotopic analysis, but this sample is not part of the currently funded study.

4. Results

The THg concentrations of samples collected along the longitudinal transect of the South River are presented in Figures 1 & 2. The concentration profiles are in general agreement with previous studies. The bank soil THg concentrations peak at 65 µg/g directly downstream of Outfall 011, while the sediment concentrations peak at 45 µg/g around RRM 3.5, with concentrations decreasing dramatically farther downstream (Fig. 1). Suspended (particulate) and dissolved fractions reach peak concentrations downstream of the plant outfall at RRM 8.5, with THg concentrations of 93.0 ng/L and 9.69 ng/L respectively (Fig. 2).

The longitudinal variation in $\delta^{202}\text{Hg}$ values of the samples collected in the South River is shown in Figure 3. 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. At site RRM 22.1, $\delta^{202}\text{Hg}$ values of the bank soils and streambed sediments trend toward a mixture between regional background and contaminated source signals.

At the Outfall 001 site, both suspended and dissolved Hg loads exhibit $\delta^{202}\text{Hg}$ values much lower than those observed within the streambed sediments and bank soils (-1.06‰ and -1.22‰, respectively). For the suspended load, mixing to the industrial source Hg isotopic value occurs at RRM 1.5, after which point the $\delta^{202}\text{Hg}$ values of the suspended load remain relatively constant. We hypothesize that this pattern is due to the influence of regional background Hg on Hg isotope composition, because Hg entrained in the water column takes time to equilibrate with Hg in the sediment load. Even after such mixing has occurred, the dissolved Hg load maintains significant negative $\delta^{202}\text{Hg}$ values relative to the suspended load (between -0.30‰ and -0.09‰) that remains relatively consistent as water moves downstream. Our current hypotheses for this pattern are discussed in detail below.

The longitudinal change in the $\Delta^{199}\text{Hg}$ values of the bank soils and sediments along the longitudinal transect is depicted in Figure 4. 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 sites impacted by contamination (0.04‰ for sediment and 0.03‰ for bank soil). In the initial reach below the plant outfall (Outfall 011 site), the suspended load shows a slightly positive $\Delta^{199}\text{Hg}$ value ($\sim 0.10\text{‰}$), but after this reach there is little variation in isotopic composition between the suspended load, sediments, and bank soils downstream. Hg in the dissolved fraction has $\Delta^{199}\text{Hg}$ values near 0.0‰ for most of the study area, similar to the suspended load. However, the dissolved fraction shows significantly elevated $\Delta^{199}\text{Hg}$ values in two locations, RRM 1.5 and SFR-01, suggesting photochemical reduction of Hg is occurring in the reaches upstream of these sites. Increased amounts of photochemistry may be occurring within these reaches due to relatively less tree canopy cover and relatively wider/shallower river channels.

The isotopic composition of the groundwater wells sampled from the piezometers at site RRM 3.5 and the Wertman Pond samples are shown on detailed longitudinal profiles in Figures 5 and 6. The Wertman Pond (floodplain pond) bank soil ($\delta^{202}\text{Hg} = -0.68\text{‰}$ and $\Delta^{199}\text{Hg} = 0.04\text{‰}$), and sediment ($\delta^{202}\text{Hg} = -0.58\text{‰}$ and $\Delta^{199}\text{Hg} = 0.04\text{‰}$) samples appear to be isotopically similar to mercury in sediment and suspended in the water column directly upstream ($\delta^{202}\text{Hg} = -0.60\text{‰}$ and $\Delta^{199}\text{Hg} = 0.03\text{‰}$), consistent with the hypothesis that movement of sediment loads during flood events is a source of mercury to floodplains. At RRM 3.5, we observe that the dissolved Hg load in bank groundwater is isotopically distinct in both $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ from the suspended load for both of the sampled wells. We hypothesize that this is the result of two processes occurring simultaneously. The first is that the positive $\delta^{202}\text{Hg}$ shift between suspended and dissolved bank groundwater Hg is in agreement with sorption of Hg in the dissolved phase to Fe-oxides⁴, an interpretation that is supported by our observation of Fe-rich waters during the piezometer sampling. The second process that we hypothesize is occurring is that Hg, which has been photochemically reduced in surface water within the stream channel, appears to be flowing through the hyporheic zone, mixing with Hg in groundwater within the banks, and resulting in elevated $\Delta^{199}\text{Hg}$ values of the Hg within the groundwater.

5. Preliminary Conclusions

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 contaminated site, and this significant isotopic difference allows for the tracing of the contamination-derived Hg throughout the South River fluvial system. This pattern is observed for each of the sample types we have analyzed so far.

Hg in the suspended fraction preserves the background isotopic signal below the plant outfall and slowly approaches the industrial value ~ 2 miles downstream, after which it appears to be sourced from both sediments and bank soils. This pattern is in agreement with the current working hypothesis that the IHg is entering the fluvial system from contaminated bank soils.

Hg in the dissolved load is isotopically distinct from Hg in the suspended load, with a consistent negative $\delta^{202}\text{Hg}$ offset. One might suspect that this pattern is caused by sorption of the dissolved Hg to thiol-bearing ligands or Fe-oxides and that sorption is inducing an isotopic equilibrium fractionation between dissolved and suspended Hg fractions. However this hypothesis can be ruled out because it does not agree with the expected sign of MDF observed in experimental studies documented in the literature^{4,5}. Instead, our current hypothesis is that Hg in

different size fractions (suspended vs. dissolved) is associated with differing ligands, and bonding to these differing ligands induces differing amounts of MDF. The smallest size fraction (referred to as dissolved, but simply $<0.45\ \mu\text{m}$) is likely to be associated with DOC, which can contain numerous types of ligands with high affinity for Hg. It is also possible that fractionation between the dissolved phase and other phases is not occurring; rather the observed isotopic variation is the result of end-member mixing between isotopically distinct Hg associated with different size fractions. However, we currently have no evidence for two different Hg isotope sources that partition into different size fractions. Ongoing analysis of the plant wastewater treatment outfall (Outfall 001), which is beyond the scope of this initial study, may help provide additional evidence to elucidate this question.

The dissolved Hg load in filtered surface water is isotopically similar in $\Delta^{199}\text{Hg}$ to the suspended load, with the exception of two reaches with elevated $\Delta^{199}\text{Hg}$ values. This indicates that in these two reaches, (0.25-1.7 RRM and below RRM 22.1) photochemical reduction of Hg and loss of Hg^0 is playing a role in the biogeochemical cycling of Hg. Given the magnitude of $\Delta^{199}\text{Hg}$ values, experimental calibrations in the literature³ allow us to estimate that $\sim 30\%$ of Hg^{2+} was photochemically reduced and lost through evasion in these reaches.

The dissolved Hg load in bank groundwater is isotopically distinct in both $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ from the suspended load within bank groundwater. The observation of +MIF within the bank groundwater indicates that surface water derived Hg is infiltrating the hyporheic zone and isotopic mixing is occurring with bank groundwater Hg. This observation also implies that with further sampling and analysis efforts, the influence of bank groundwater on dissolved Hg in river water may be traceable and it may be possible to differentiate groundwater versus surface water derived Hg.

Finally, it appears possible that Hg isotope analysis may be useful for identifying the fraction of Hg that is available for methylation within the South River due to the significant isotopic difference between Hg in the dissolved load and Hg in sediment/suspended load. Further work will be needed to chemically separate methyl mercury from total mercury⁶ in South River samples to better understand the processes that control methylation. In addition, further insight into the parameters controlling movement of inorganic Hg into the South River stream channel should be obtainable through more intensive sampling and isotopic analysis of Hg deposited within the banks and floodplains, as well as in groundwater and hyporheic zone.

References

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Figures

Figure 1- THg Concentration of Bank Soils and Streambed Sediments Along Longitudinal Transect of South River

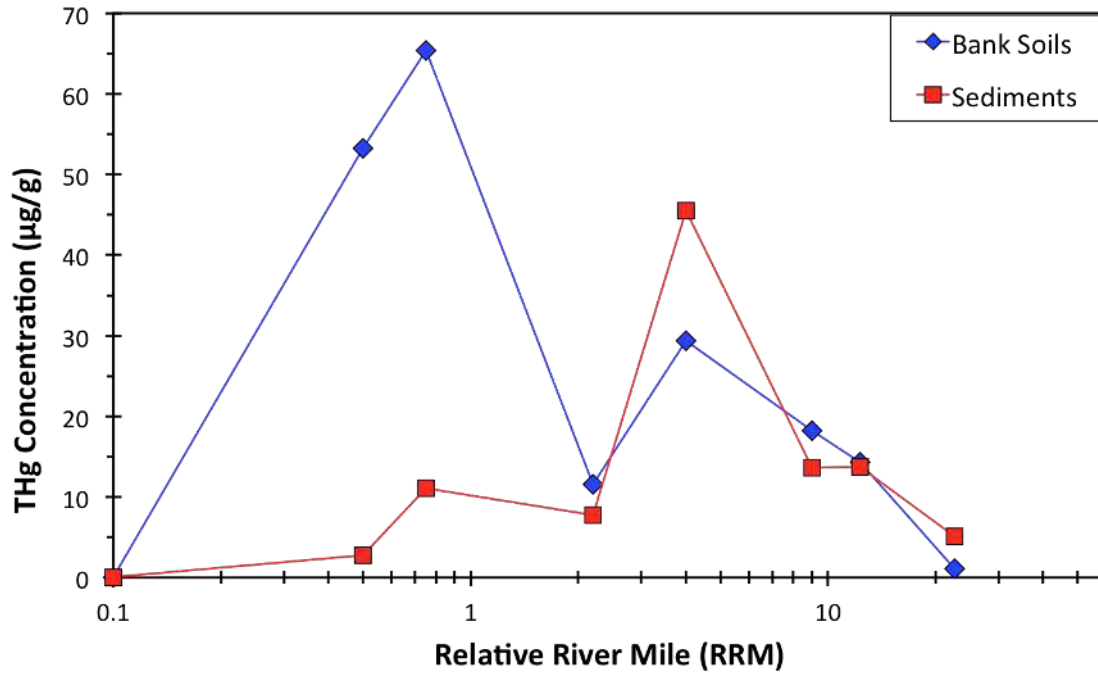


Figure 2- THg Concentration of Filtered Surface Water Along Longitudinal Transect of South River

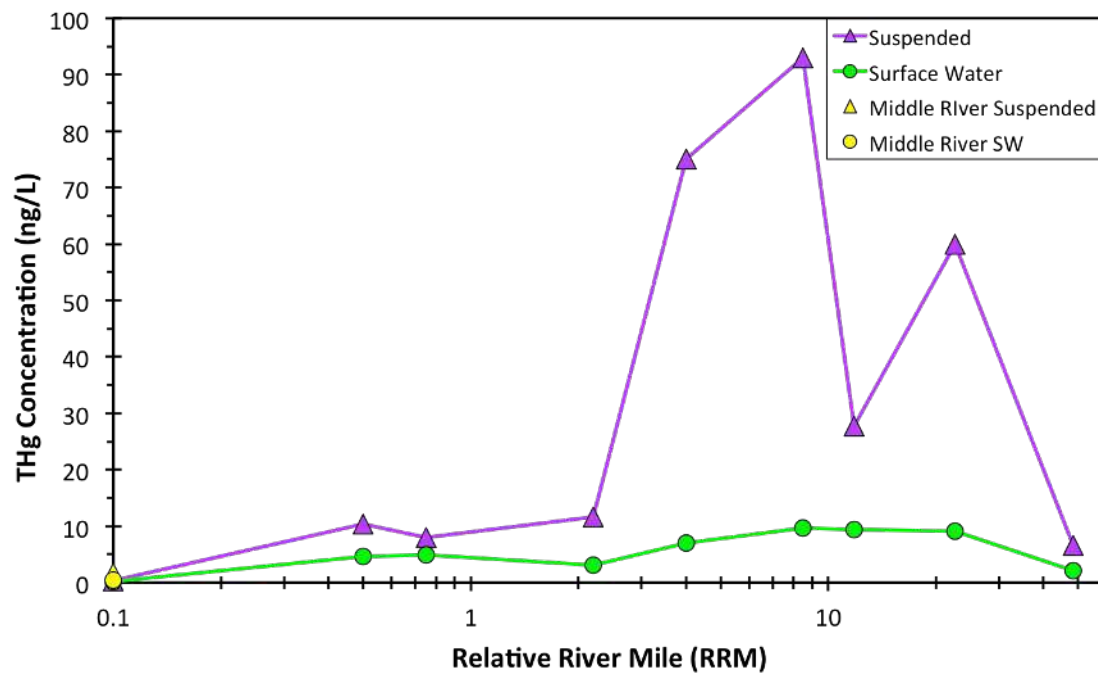


Figure 3 - $\delta^{202}\text{Hg}$ Values Along a Longitudinal Transect of the South River

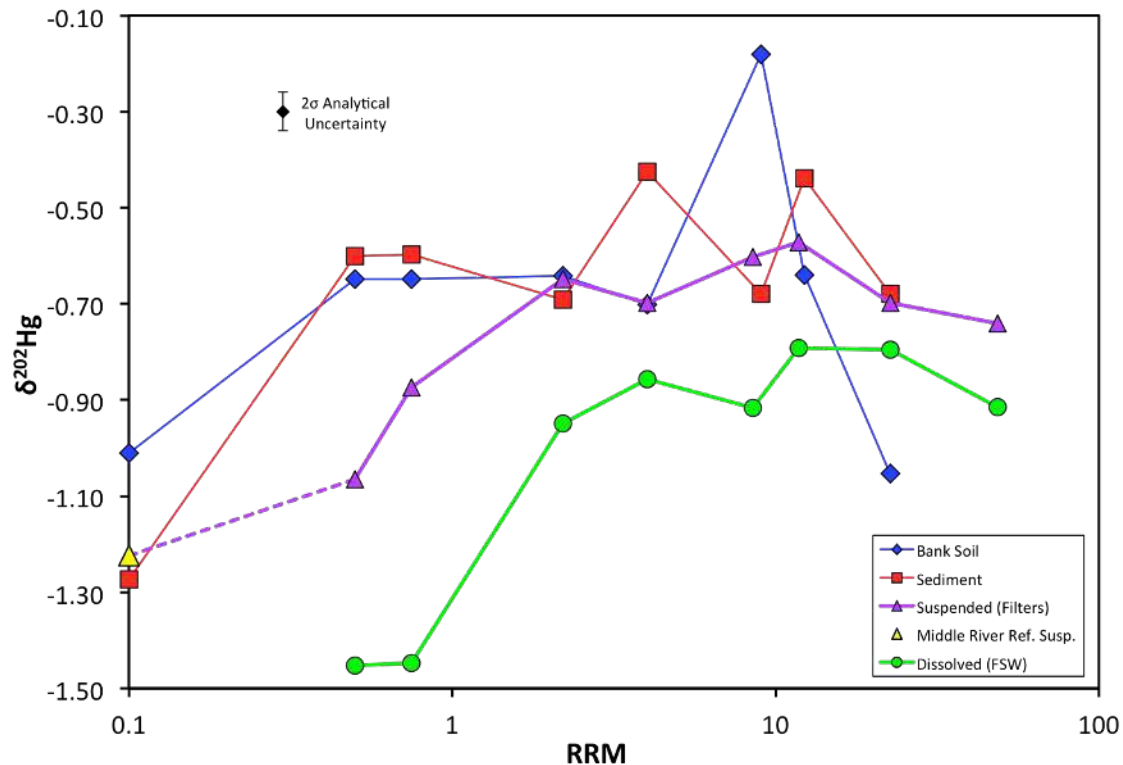
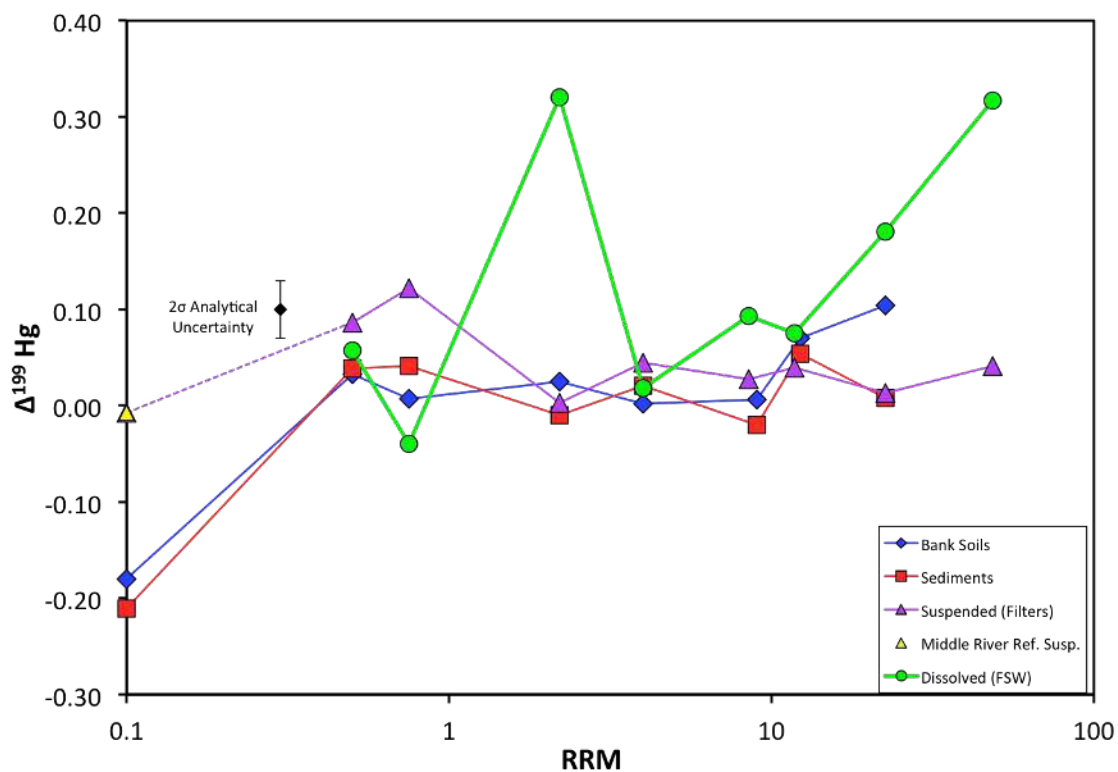


Figure 4 - $\Delta^{199}\text{Hg}$ Values Along a Longitudinal Transect of the South River



6202Hg

RRM

Legend:

- Bank Soil
- Sediment
- Wertman Pond Sed
- Wertman Pond BS
- Suspended (Filters)
- Wertman Pond Susp.
- RRM 3.5 Wells
- RRM 3.5 0.2um
- RRM 3.5 Wells Dis
- Wertman Pond Dis
- Dissolved (FSW)

Figure 1 is a scatter plot showing the relationship between the Redox Ratio (RRM) on the x-axis and the difference in $\Delta^{199}\text{Hg}$ on the y-axis. The x-axis is logarithmic, ranging from 1 to 10. The y-axis ranges from -0.03 to 0.13. Data points are categorized by sample type: Bank Soils (blue diamonds), Sediments (red squares), WP Sed (green triangles), WP BS (black circles), Suspended (Filters) (purple triangles), Wertman Pond Susp. (green triangles), RRM 3.5 Wells (grey circles), RRM 3.5 0.2um (orange squares), RRM 3.5 Wells Dis. (green circles), and Dissolved (FSW) (green circles). The plot shows a general trend where $\Delta^{199}\text{Hg}$ increases with RRM, with a notable peak around RRM 10 for Bank Soils and Sediments.