

Geochemical Characterization of Mercury-Bearing Riverbank Sediments and Soils from the South River, Virginia (USA)

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Introduction

The sediments beneath and adjacent to the South River, near Waynesboro, VA, contain elevated concentrations of mercury (Hg). As these sediments erode, Hg-bearing particles enter the river and can release Hg to the water in dissolved or particulate forms. Flooding and precipitation events can induce infiltration of water through soils and sediments and potentially lead to additional input of Hg to the river. This infiltration can lead to changes in soil moisture content which can subsequently promote a series of reactions in the aqueous and solid-phase chemistry and changes in Hg speciation and transport. Studies are being conducted at the University of Waterloo to evaluate the extent of Hg release through sediment resuspension events and through enhanced groundwater transport associated with precipitation and flood events. An overview of the experiments that have been completed or are underway is provided. The results of the studies will aid in the prediction of Hg release to the river and design of remedial systems.

The studies include 1) measurements to characterize the bulk sediment to determine the composition of sediment particles and potential for Hg binding, 2) experiments to provide an indication of Hg release as sediments are eroded and enter the river, and 3) leaching experiments to evaluate Hg release under fully saturated and variably saturated conditions with input solutions of different compositions including river or acid rain water. Sediment and soil samples were collected from locations with elevated concentrations of Hg, and from sites with low concentrations of Hg (RRM 0.25, 2.4 and 3.4). The low-Hg samples were selected to quantify the potential for Hg release from sections of the river which represent a large portion of the river channel. Additional samples were collected from the river floodplain at locations with known elevated concentrations of Hg.

Specific tools that are being applied in the studies include:

chemical analyses to determine masses of Hg, other elements and nutrients;

mineralogical analyses, including optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersion x-ray analyses (EDXA), to determine particle morphology, bulk mineralogy, and chemical composition of particles;

synchrotron radiation-based X-ray absorption spectroscopy (XAS) to determine oxidation states and nature of binding of Hg to other elements;

sequential extraction assays to determine the stability of Hg when sediments are exposed to different reagents;

batch resuspension tests to evaluate the mass of Hg released when sediments are mixed with South River water;
long-term saturated column tests to evaluate Hg leaching under saturated flow conditions;
humidity test cells to simulate wet / dry cycling when sediments are exposed to South River water and simulated acid rain; and
geochemical modeling

The results obtained from these and other tools will be integrated to develop an improved understanding of Hg behavior at the South River site and processes leading to its release, transport and attenuation, and potential availability for methylation.

Sample Collection Locations

Sediment and soil samples were collected from the riverbank along the South River and within the floodplain (Figure 1). These samples cover a range in concentration of total solid-phase Hg, from near background values to concentrations representative of the highest concentrations observed in the study area.

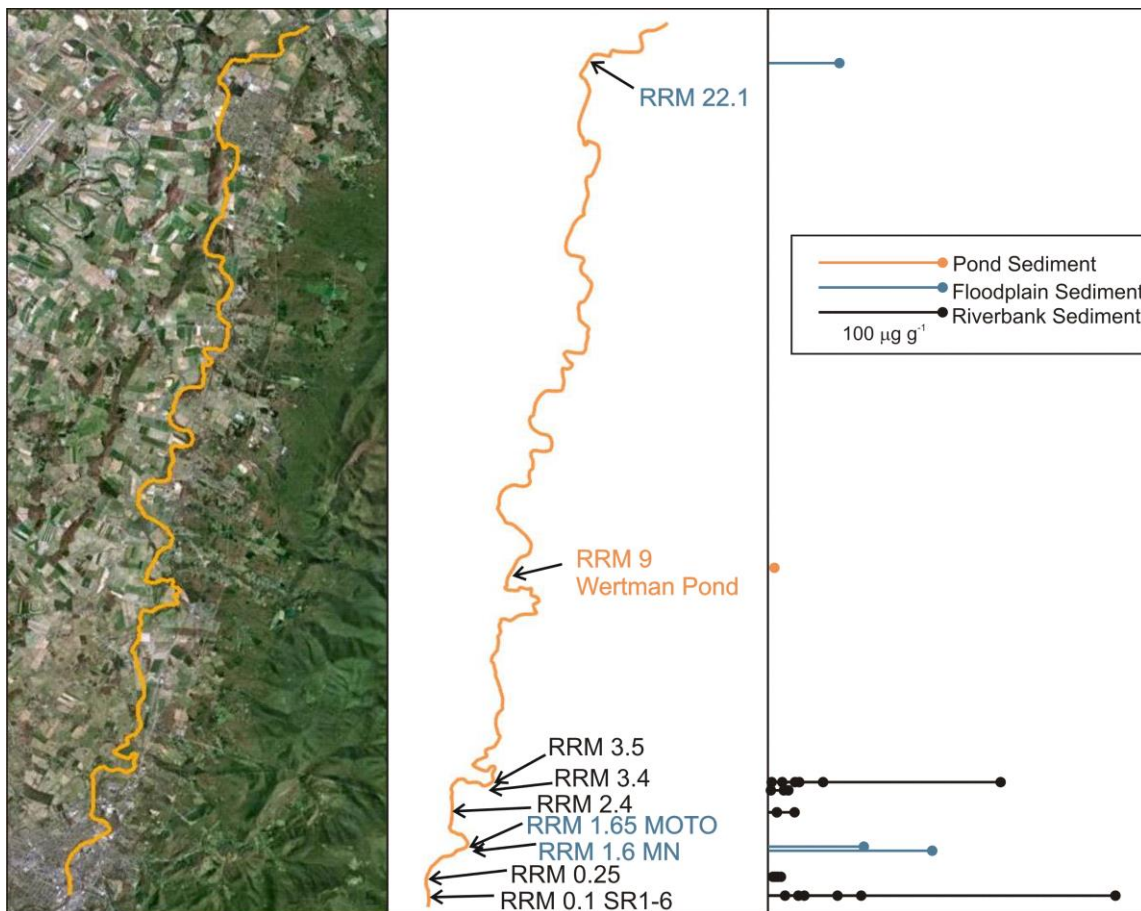


Figure 1. Map showing sampling locations, expressed as relative river mile (RRM) downstream from Hg source area, type of sample, and concentrations of total Hg expressed on a dry weight basis.

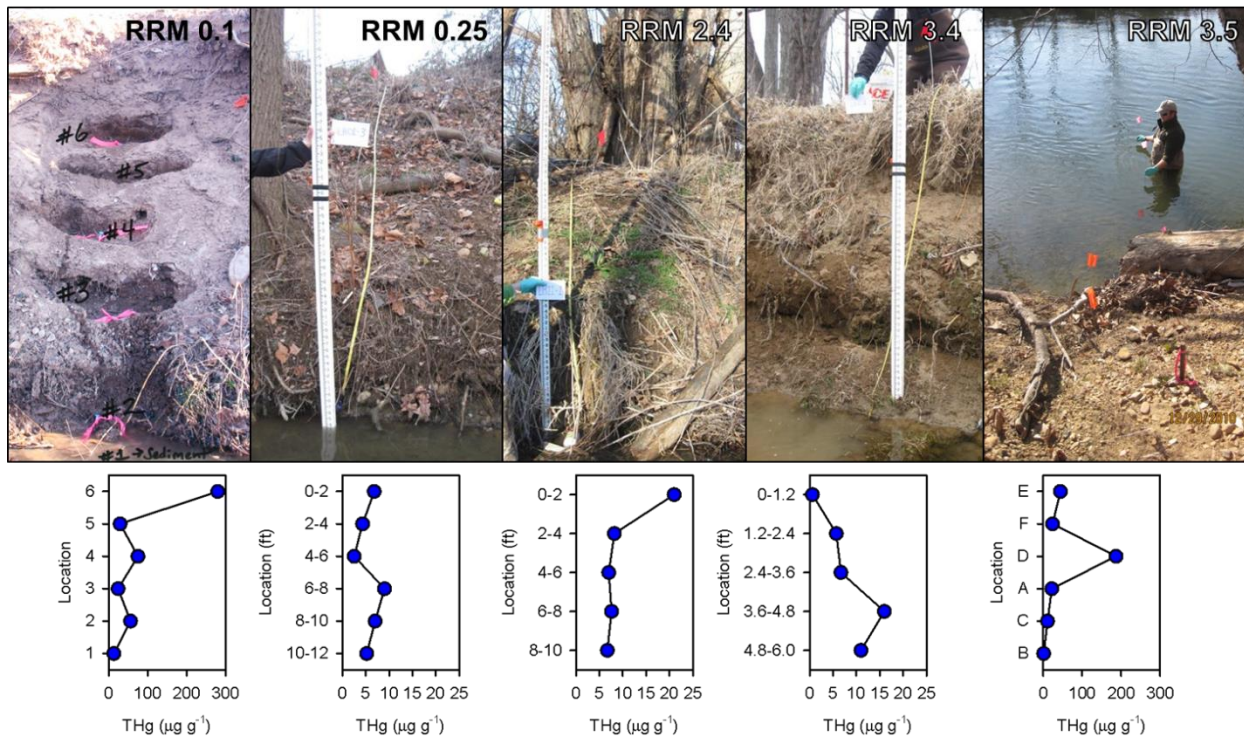


Figure 2. Photographs showing sample collection locations (top) and corresponding THg concentrations (bottom) at transects at RRM 0.1, 0.25, 2.4, 3.4, and 3.5. These locations were selected for more detailed study due to the presence of both low and elevated concentrations of Hg.

Overview of Results and Status of Studies

Solid-phase Chemical Analyses: Chemical analyses of solid-phase samples indicate highly variable concentrations of Hg at the site and generally elevated concentrations of Fe (Table 1).

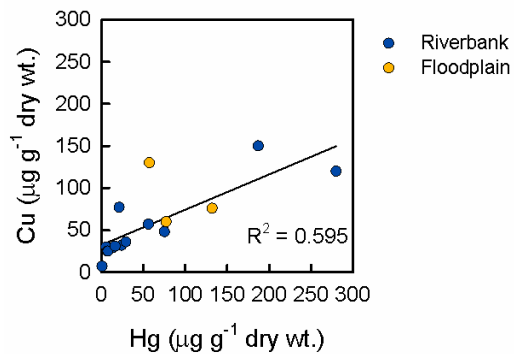


Figure 3. Correlation between total Hg and total Cu present in the riverbank and floodplain sediments.

Concentrations of Hg in the riverbank sediments ranged from 0.6 $\mu\text{g g}^{-1}$ to 280 $\mu\text{g g}^{-1}$, and in the floodplain sediments from 57 $\mu\text{g g}^{-1}$ to 132 $\mu\text{g g}^{-1}$. The concentrations of Hg are correlated strongly with solid-phase Cu concentrations, consistent with the chalcophile nature of these two elements (Figure 3).

Table 1. Concentrations of Hg and other elements in selected samples collected from the study area, including sample ID and location reported as relative river mile. For transects 0.25, 2.4 and 3.4 only those sediments which were chosen for column experiments are shown.

| Sample ID | Location (miles) | Hg | Cu | Fe | K | Mg | Mn | Ni | Pb |
|-----------|------------------|-----------------------------------|-----|-------|------|-------|------|-----|-----|
| | | $\mu\text{g g}^{-1}$, dry weight | | | | | | | |
| SR1 | 0.1 | 13 | 29 | 12000 | 1500 | 710 | 140 | 8.8 | 14 |
| SR2 | | 56 | 57 | 20000 | 1000 | 870 | 320 | 14 | 23 |
| SR3 | | 24 | 32 | 29000 | 2000 | 1200 | 340 | 10 | 13 |
| SR4 | | 75 | 48 | 17000 | 1000 | 910 | 310 | 9 | 23 |
| SR5 | | 29 | 36 | 20000 | 1300 | 1100 | 420 | 13 | 26 |
| SR6 | | 280 | 120 | 16000 | 820 | 930 | 300 | 8.5 | 23 |
| 10-12' | 0.25 | 5.2 | 30 | 14000 | 1000 | 13000 | 240 | 9.3 | 82 |
| 0-2' | | 6.8 | 25 | 16000 | 990 | 2300 | 320 | 9.4 | 32 |
| MN-38 | 1.6 | 132 | 76 | 27000 | 1800 | 1300 | 460 | 10 | 30 |
| MOTO | 1.65 | 77 | 60 | 14000 | 1600 | 760 | 290 | 6.3 | 18 |
| 6-8' | 2.4 | 7.6 | 25 | 25000 | 1900 | 2100 | 560 | 13 | 20 |
| 0-2' | | 21 | 77 | 22000 | 1200 | 1900 | 380 | 13 | 54 |
| 3.6-4.8' | 3.4 | 16 | 31 | 15000 | 1100 | 1100 | 240 | 8.0 | 29 |
| 0-1.2' | | 0.6 | 7.1 | 17000 | 910 | 1200 | 390 | 7.2 | 6.0 |
| SRD | 3.5 | 187 | 150 | 16000 | 760 | 1200 | 230 | 8.2 | 21 |
| RRM 22.1 | 22.1 | 57 | 130 | 24000 | 780 | 1100 | 1500 | 22 | 27 |

Mineralogical Analyses: Mineralogical studies are currently underway and include a variety of techniques to identify the morphology and composition of particles in the sediments and soils in samples collected along the South River and within the floodplain. A number of samples collected from RRM 0.1 and RRM 3.5 were prepared for analysis using SEM, TEM and other methods. Preliminary results of analyses of river bank sediments indicate that the dominant phase observed in polished thin sections was quartz. The next most common phases consisted of agglomerates of Al-rich silicates (most likely clays) and fragments of quartz, feldspar, and Fe-silicate (much less common). Lesser quantities of mid-to-highly weathered feldspars (orthoclase/microcline and albite) were observed in agglomerates, but also as separate grains. Other particles were composed of Fe and Ti (hydr)oxides. Elevated concentrations of Hg were observed in fine-grained particles enriched in C, S, and often Al and alkali elements such as Na, K, and Ca which were attached to agglomerates. These studies will be continued to further quantify the nature of the Hg associations.

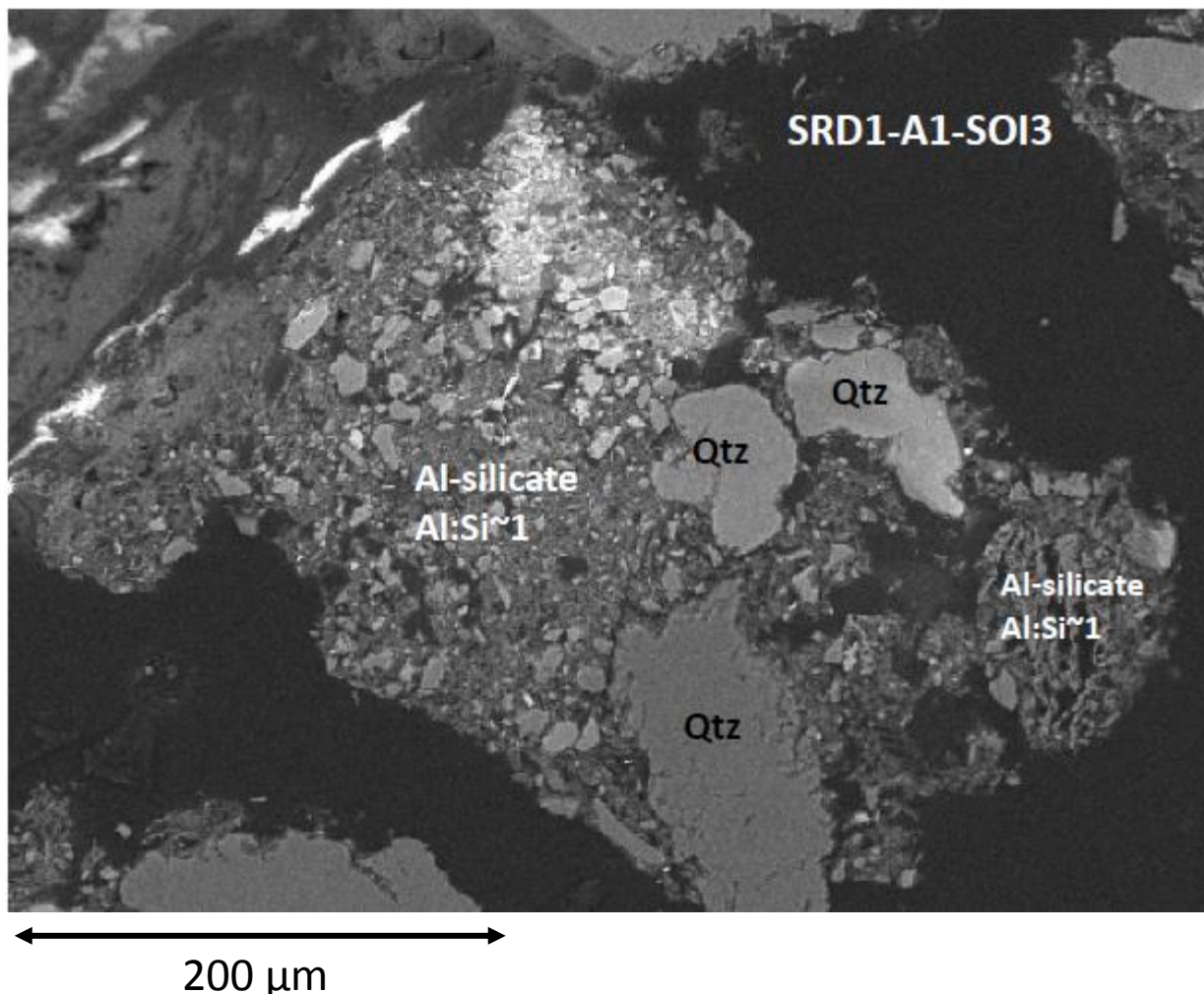


Figure 4. Example SEM image of bank sediment collected from location RRM 3.5 – SRD showing typical grain morphology observed in thin section samples.

Synchrotron Radiation Analyses: Synchrotron radiation-based XAS techniques were employed to characterize the form of Hg in the bank sediments and floodplains soils. Six samples from RRM 0.1 (SR1 to SR6), five samples from RRM 3.5 (SRA, SRB, SRC, SRE, and SRF), and floodplain samples from the motocross area at RRM 2.4 (labelled MOTO) and RRM 22.1 were analyzed on Beamline 13-BM-D-GSECARS at the Advanced Photon Source (Argonne National Laboratory, Lemont, IL, USA). A 13-element Ge detector (Canberra Industries Inc., Meriden, CT, USA) and a defocused beam measuring approximately 1000 x 300 μm was used for collection of XANES spectra for Hg. Data processing was performed with the program ATHENA (Ravel and Newville, 2005). XANES spectra were collected on the same beamline for Hg bearing standards (Figure 5).

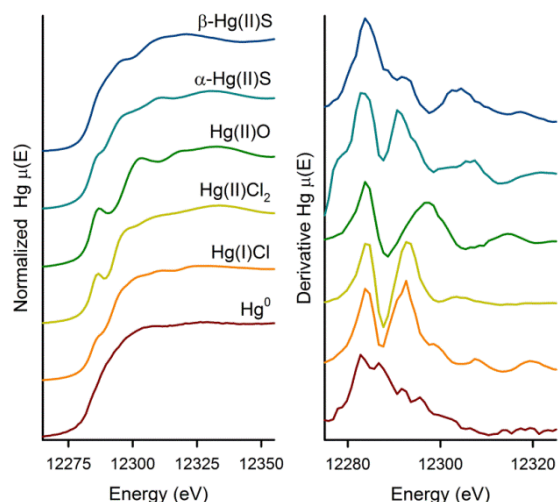


Figure 5. Hg XANES reference spectra for selected standards.

The minimum concentration for analysis of Hg by XANES was approximately $100 \mu\text{g g}^{-1}$. As such, Hg was difficult to detect in many of the samples. Mercury XANES spectra were obtained for the lowest and highest elevation samples at RRM 0.1 (SR1 and SR6), the floodplain sample at RRM 2.4 (MOTO), a high-Hg sample at RRM 3.5 (SRD), and the floodplain sample at RRM 22.1 (Figure 6).

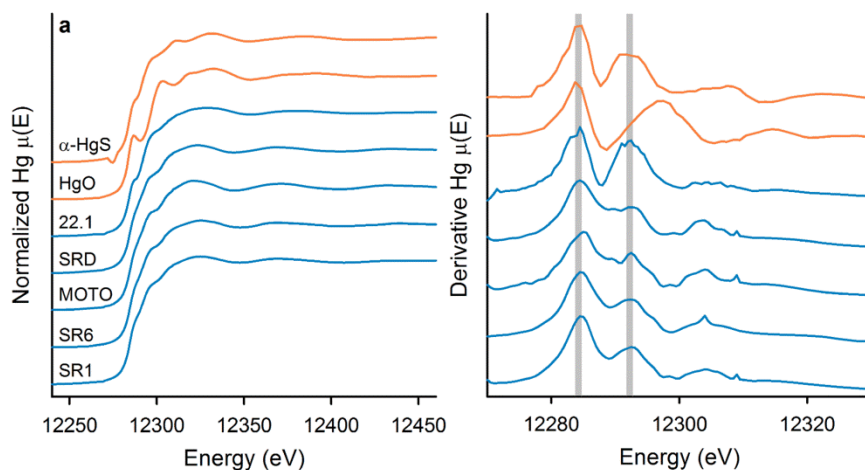


Figure 6. Hg L-edge XANES spectra for selected standards and sediment samples collected from the riverbank and floodplain. The grey lines on the Hg XANES derivative plot show first and second peak locations typical of cinnabar [α -HgS]

At each location, Hg appeared to be bound to sulfur with spectra resembling either cinnabar or metacinnabar and possibly as Hg bound to thiol groups in organic matter. A detailed analysis of the extended fine structure region would be required to differentiate between inorganic and organic Hg-S bonding, however the spectra collected in this study were too weak to perform this analysis.

Sequential Extraction Assays: Sequential extraction analyses were conducted on river bank and floodplain samples to assess the potential bioavailability of Hg through a five-step extraction

process: deionized water (targets HgCl_2 , HgSO_4), 0.1 M CH_3COOH + 0.01M HCl at pH 2 (targets HgSO_4 , HgO , adsorbed Hg), 1M KOH (targets organo-chelated Hg, Hg_2Cl_2), 12M HNO_3 (targets Hg^0 , thiol-bound Hg), and aqua regia (targets HgS , HgSe , HgAu) (Bloom et al., 2003). These extractions can be used to infer the presence of target phases, but do not provide definitive identification of these phases. The results of the extractions indicate release of Hg under all five extraction steps for all samples (Figure 7), suggesting a range in potential availability of Hg for biological uptake and other reactions. The F4 and F5 fractions dominate the Hg forms for the majority of the sediments, though for the low-Hg samples collected from RRM 0.25 and RRM 2.4 there is a greater proportion of the F3 fraction, especially in the sediments from locations further away from the base flow of the river. The analyses, however, are static tests and only represent release of Hg for sediment:extract ratios used in the assays.

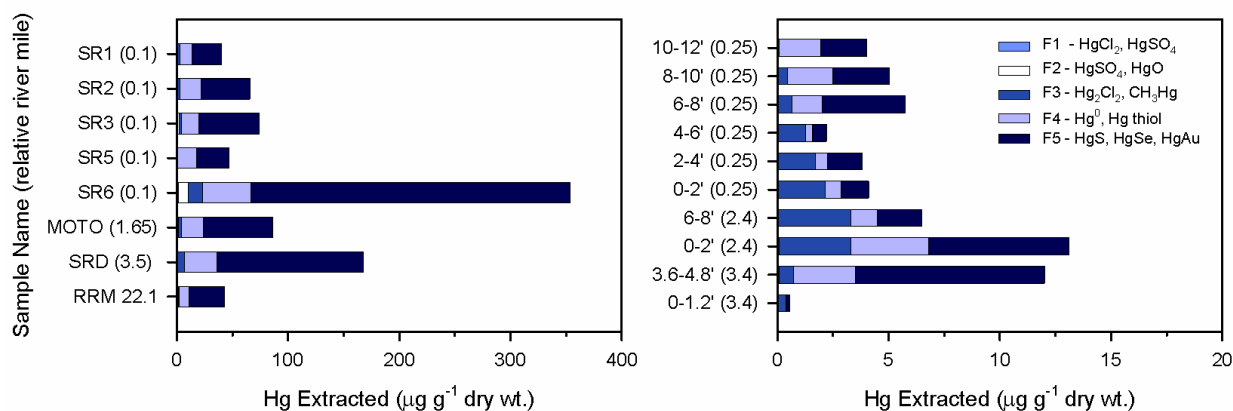


Figure 7. In-house Hg sequential chemical extraction data for soil and sediment samples. Left: High-Hg samples, and Right: Low-Hg samples. Note: The presence of all five fractions for all samples, but the predominance of the F4 (targeted phases are Hg^0 and thiol-bound Hg) and F5 (targeted phases are HgS , HgSe and HgAu) fractions.

Resuspension Tests: A modified elutriate test protocol described in the EPA Inland Testing Manual (US EPA, 1996) was employed to determine the potential for Hg leaching as sediment erodes from the riverbanks into the river from the low-Hg sediments and compared to the higher Hg sediments results determined previously. Sediment and South River water were combined at 40:1, 20:1, 10:1 and 4:1 ratios and gently agitated for 30 minutes. The aqueous supernatant was filtered (0.45 µm) and the samples analysed for Hg and other chemical parameters.

Concentrations of Hg were observed to generally increase with a decrease in liquid-solid ratios (Figure 8). Concentrations of Hg ranged from 0.2 to 80.2 µg L⁻¹ for water in contact with sediment collected along the riverbank, and ranged from 6 to 30 ng L⁻¹ for cobblestone samples collected within the riverbed (SRB and SRD). The highest concentrations of Hg were observed for the SR6 sediment. The greatest aqueous THg released from the low-Hg sediments of 1020 ng L⁻¹ was observed with the sediment from RRM 2.4 (0-2') with a 1:4 sediment to SRW ratio. The resuspension tests show that of the low-Hg sediments, the sediments that could potentially leach large amounts of Hg were: RRM 0.25 (10-12'), RRM 2.4 (0-2'), RRM 3.4 (3.6-4.8'). Based on the resuspension test results, two sediment samples each from the 0.25, 2.4, and 3.4 transects were selected for saturated flow-through column experiments.

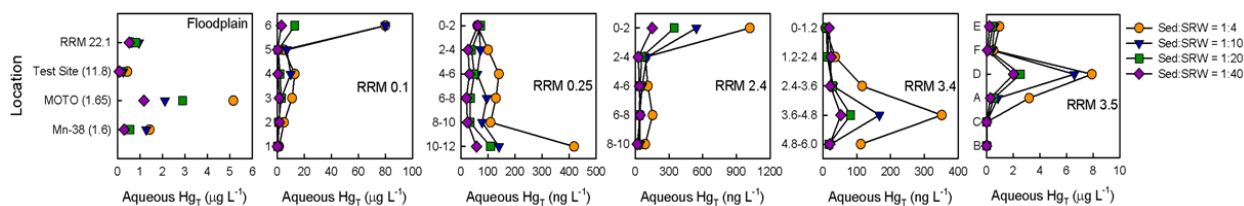


Figure 8. Concentrations of Hg in 0.45 µm filtered water samples released during sediment resuspension experiments reported as a function of the mass ratio of water and sediment.

Leaching of Hg under Saturated Flow Conditions: Saturated flow column experiments provide a direct measurement of the release of Hg as water flows through sediment at solid:water ratios representative of field conditions. Sediments from transects 0.25, 2.4 and 3.4 were packed into columns and the water was pumped at a flow rate of 100 mL week⁻¹ yielding calculated average linear velocities ranging from 16 to 40 cm d⁻¹.

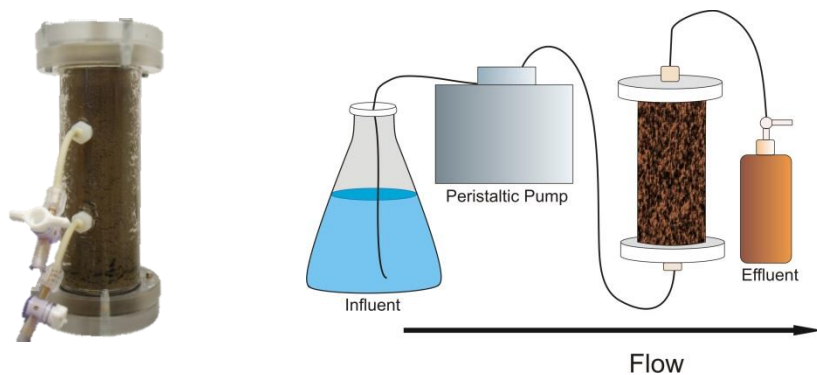


Figure 9: Photograph of column packed with sediment collected from RRM 2.4 (6-8') (left) and schematic diagram of experimental set-up (right).

Analyses of water samples collected over the first 50 pore volumes of flow from the low-Hg columns (Figure 10) indicate that the effluent from RRM 0.25 (10-12') had the highest concentrations of THg. Relatively low concentrations of solid-phase Hg were observed at this site, and low concentrations of Hg were leached in the resuspension tests, suggesting that there is a poor correlation between leaching under dynamic flow conditions and the total Hg concentrations and leaching during resuspension tests. In all three low-Hg transects the highest concentrations of Hg were observed in the effluent from the columns containing sediment obtained closest to the base flow of the river rather than the sediment collected from higher up the bank. The maximum concentrations of MeHg of 25 ng L⁻¹ were observed in the effluent of the column containing sediment from RRM 2.4 (6-8') followed by 0.25 (0-2') where a maximum of 8.8 ng L⁻¹ of MeHg was observed.

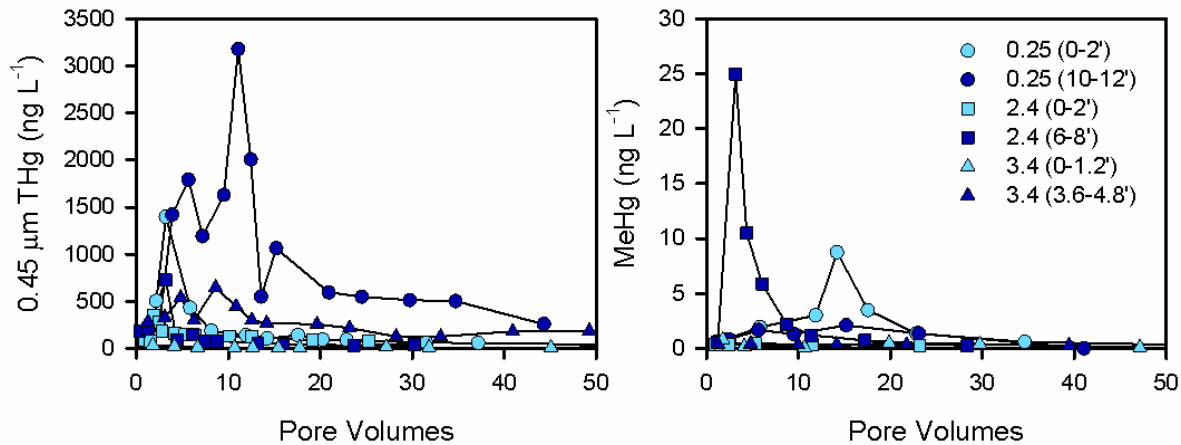


Figure 10: Concentrations of 0.45 µm filtered Hg in the effluent from the columns containing low-Hg sediments (left) and the corresponding effluent MeHg concentrations (right).

Comparison of Hg Release from a Range of Sediment Samples: The concentrations of Hg in the effluent collected from the low-Hg saturated column experiments were compared to the concentrations observed in column experiments conducted with sediment containing elevated concentrations of Hg. The greatest cumulative release of Hg was observed for columns containing sediments collected from locations closest to the base flow of the river (*e.g.*, RRM 0.25 10-12' and RRM 0.1 -3) (Figure 11). The release of Hg under saturated flow conditions appears to be directly correlated to the degree of saturation at the time of sample collection.

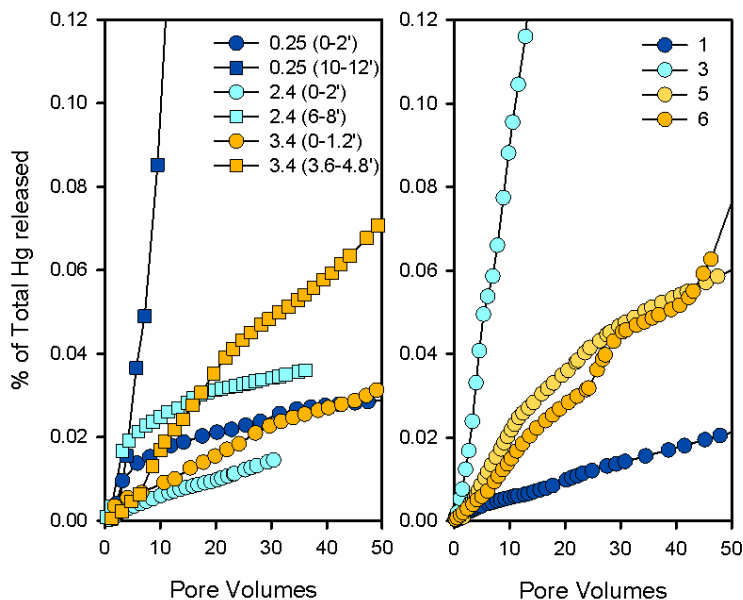


Figure 11. Comparison of cumulative Hg observed in the effluent of the low-Hg columns from low-Hg locations (left) and high-Hg locations (RRM 0.1; right).

Release of Hg under Variable Moisture Contents: Changes in moisture contents can lead to the generation of alternating oxidizing and reducing conditions, which can promote weathering reactions and, in turn, induce changes which may influence Hg release. Humidity test cell experiments were conducted following a standardized protocol (ASTM, 2012) to promote cyclic changes in moisture contents. Slight modifications to the procedure were made to evaluate the influence of input solution composition and holding times on Hg release. Simulated acid rain water (pH 4.6) was used for the input solution for the floodplain soils (MOTO and RRM 22.1) and South River water was used as input solution for the river bank sediments (RRM 0.1 SR6 and RRM 3.5 SRD). In addition, simulated acid rain water was used for the input solution for a second column containing SR6. After addition of the input solutions, the cells were exposed to dry air and then wet air and then rewet on a weekly basis. The cells with river sediments were allowed to stagnate for 4 days prior to exposing to dry air and wet air, whereas the cells with floodplain soils were not allowed to stagnate between flushing events.

The concentrations of unfiltered Hg in the humidity test cell effluent initially exceeded $150 \mu\text{g L}^{-1}$ for all three columns with simulated acid rain water as the input solution (Figure 12). The concentrations then declined steadily for the two soil samples (MOTO and RRM 22.1), approaching a few $\mu\text{g L}^{-1}$ by the end of week 60 (Figure 11, subplots a and b). For the SR6 sediment, the concentrations in the effluent were more sporadic exceeding $100 \mu\text{g L}^{-1}$ in several samples during the experiment (Figure 11, subplot c). For all three sediments, the concentrations of filtered Hg ($0.45 \mu\text{m}$ filter passing fraction) released from the floodplain soils were less than $10 \mu\text{g L}^{-1}$ and generally averaged around $3 \mu\text{g L}^{-1}$. The majority of the Hg ($> 80\%$) was released in the colloidal form ($>0.45 \mu\text{m}$ fraction).

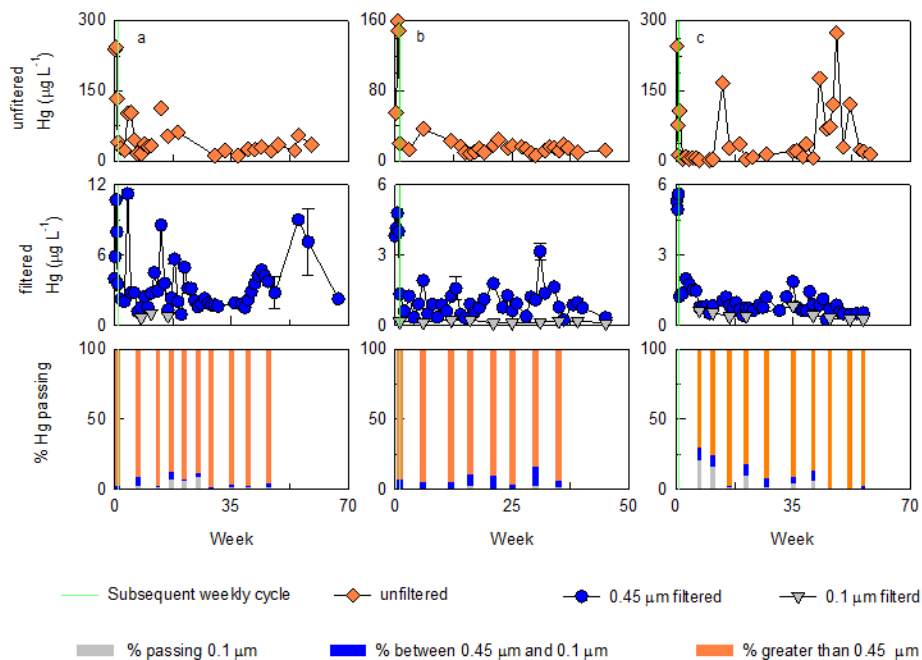


Figure 12. Release of Hg from humidity test cells packed with floodplain soils and riverbank sediment and flushed with simulated acid rain water, including unfiltered Hg, filtered Hg, and Hg filter fractions. a) MOTO soil, b) RRM 22.1 soil, and c) RRM 0.1 SR6 riverbank sediment.

For the cells flushed with South River water (Figure 13), the concentrations of unfiltered Hg and filtered Hg were substantially less than observed for cells with acid rain input (Figure 12). The concentrations of unfiltered Hg approached $50 \mu\text{g L}^{-1}$ from SR6 flushed with the South River water. The concentrations of dissolved Hg (0.45 μm filter passing fraction) from SR6 and SRD were approximately 500 ng L^{-1} as the experiments progressed. The majority of the Hg was present in colloidal forms for both columns during the subsequent weekly cycles.

These results suggest that the transport of Hg in the form of fine-grained particles was likely enhanced due to the combination of both rapid flow rates and alternating wet/dry conditions in the cells. The transport of Hg was greater for the columns with the acid rain water as the input solution. A comparison of the results suggest that the acidic conditions generated in the column with simulated acid rain water as input solution may have promoted the disaggregation of particles allowing greater transport through the sediments.

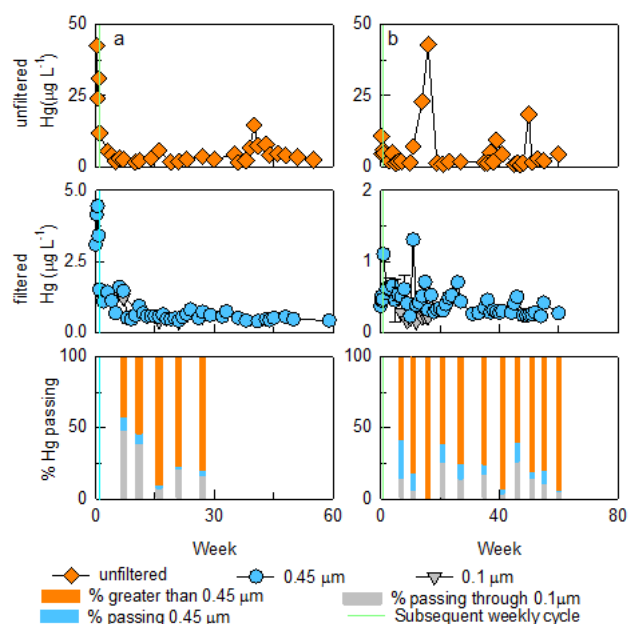


Figure 13. Release of Hg from humidity test cells packed with river bank sediment and flushed with South River water, including unfiltered Hg, filtered Hg, and Hg filter fractions. A) RRM 0.1 SR6, and B) RRM 3.5 SRD

Summary

The studies to date indicate that the distribution and speciation of Hg in the South River sediment and soils are highly variable. The Hg appears to be bound within aggregates of fine sediment particles, some of which is associated with reduced S, likely as metacinnabar. In addition to bound Hg, a portion is readily available for leaching, as indicated by the elevated concentrations of Hg observed in filtered water samples in contact with the sediment, including water collected in resuspension tests, saturated column experiments and humidity test cell experiments. In the low-Hg saturated column experiments with South River water as input solution, the release of Hg was relatively high in comparison to the concentration of Hg in the sediment (*e.g.*, RRM 0.25 (10-12') sediment). These results suggest that the potential for sediments to release Hg cannot be predicted from Hg concentrations in the sediment alone. The low-Hg sediments that were

derived from locations closest to the base flow of the South River appear to leach a greater % of the total Hg in the sediment than those derived from locations further from the water. The application of simulated acid rain water in the humidity test cell experiments also led to greater release of Hg than for South River water as an input solution. Current efforts are directed at completing the mineralogical analyses for the low-Hg and floodplain samples, completing solid-phase characterization and experiments for the new RRM 11.8 test site Hg samples, and integrating the data collected to date.

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References

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