BRIEFING PAPER (2012-2013) - BIOGEOCHEMICAL DYNAMICS OF HG FROM RIVER BANK SOILS: SOUTH RIVER, VIRGINIA

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1. Background

The understanding of redox-driven transformations and speciation of mercury (Hg) in soil and freshwater plays a critical role in the ecosystem biogeochemistry and environmental fate of this toxicant [Morel et al., 1998] (Figure 1). Methylmercury ($CH3Hg^{+}$), the major toxic form of Hg, bioaccumulates in terrestrial and aquatic trophic chains [Lawson and Mason, 1998]. The formation and destruction of $CH3Hg^{+}$ is mostly performed by microorganisms, while the methylation rate is controlled by sulfate, sulfide and dissolved organic carbon (DOC) concentrations, as well as microbial community composition [Brown, 2009]. Sulfate-reducing bacteria are vital to production of $CH3Hg^{+}$ in sediments. In contrast, divalent mercury (Hg^{2+}) exhibits affinity toward mineralogical and biological colloids, promoting its mobilization in the environment [Balogh et al., 2000]. Soils and sediments could be enriched in Hg due to geological processes, Hg accumulation from the atmosphere or due to anthropogenic activity. Generally, the key mechanisms controlling soil Hg mobilization are physical sorption/desorption of Hg^{0} and Hg^{2+} on and from soil, as well as chemical degradation of Hg-containing minerals and reduction of Hg^{2+} [Zhang et al., 2003]. Studies showed that Hg-minerals have a wide range of solubilties, with cinnabar being highly insoluble whereas Hg oxide, sulfates and chlorides are relatively soluble. Soluble Hg-containing minerals in soils are a source of Hg^{2+}, which can be converted into $CH3Hg^{+}$ by sulfate-reducing bacteria in wetland sediments and soils.

In Waynesboro (Virginia), Hg was used between 1929 and 1950 by the DuPont plant in the production of rayon acetate fiber and released into the South River. The contamination of Hg was discovered in the 1970s and remained elevated in water, soil, sediments, and biota.

2. Objectives and hypotheses

The primary goal of this study is to investigate the processes that govern biogeochemical transformation and mobilization of Hg in the historic release-age deposits (HRAD) at South River Mile (RRM) 3.5 and to characterize geochemical gradients in soils and how they change over time. The biogeochemical data will play a supporting role and will be used to further develop our understanding of the processes controlling the leaching of Hg and our conceptual model. Our over-arching hypothesis is to test if leaching of bank soils is a significant source of colloidal or dissolved inorganic Hg (IHg).

Our major specific hypotheses include the following:

(A) Soil inundation and bank saturation occur due to horizontal flow through a highly transmissive gravel zone at the base of the bank, vertical drainage of precipitation, and

upgradient groundwater flow; the relative importance of which varies temporally and seasonally.

(B) Drainage occurs predominantly through gravel zone at the base of the bank wetting an organic rich soil.

(C) The hydraulics facilitate the downward or upward movement of the capillary fringe and saturated zone through the soil horizons affecting soil redox potential, mineral dissolution, and leaching of inorganic Hg from the soil into dissolved and colloidal phases that are bioavailable.

(D) The dissolved and colloidal inorganic Hg is either directly transported to the South River or methylated within the saturated zone of the bank and subsequently released.

3. Approach

Our effort requires an interdisciplinary geochemical approach and sensor technology including a number of state-of-the-art in-situ monitoring sensors, such as custom-designed redox probes, soil moisture, temperature, pressure, and conductivity to understand the interactions between bank soil, groundwater, and river.

In October 2012, we collected two intact soil cores at RRM 3.5 to understand the distribution and concentration of Hg in the HRAD to design redox probes, and location of soil moisture/temperature probes. Core (1) was recovered about 6 ft from river bank with the total core depth of 58.5 in hitting gravel bottom. The measured water table was at 50 in below land surface (BLS). Core (2) was extracted about 2 ft from river bank with the total depth at location of 35.5 in reaching gravel bottom. However, total recovered core was 20.5 inch long due to trapped air pocket at the soil bank. The measured water table at this location was about 30 in BLS. In February 2013, we collected additional intact soil cores at four locations of the HRAD at RRM 3.5 (Figures 1 and 7). Core (1A) was collected about 6 ft from river bank. Total recovered core was 27.2 in (core 1-1A) and 26 in (core 1-2A), respectively, while total depth at location was 60 in (gravel bottom). Water table was about 45 in BLS. Core (2A) was extracted about 2 ft from river bank with the total recovered core of 22.7 in long. Total depth at location was 32 in (gravel bottom) and water table was 27.5 in BLS. Core (3A) was extracted about 25 ft from river bank with recovered cores of 31.5 in (core 3-1A), 30.6 in (core 3-2A), and 24.4 in (core 3-3A) long, respectively. Total depth at location was 89 in (gravel bottom) and water table at 67 in BLS. Core (5A) was taken 19 ft downstream from cores (1A), (2A), and (3A), and 13 ft from stream bank. Recovered cores were 30 in (core 5-1A), 24 in (core 5-2A); and 14 in (core 5-3A) long, respectively. Total depth at the location was 84 in (gravel bottom) and water table at 74 in BLS.

After the collection, soil cores were kept on ice in the cooler and subsequently transported to the freezer at the University of Delaware. In preparation for analyses, frozen soil cores were thawed at room temperature, cut into a separate sample vials (every 5 inch of core), described, dried, homogenized, weighted, sieved through a 2-mm sieve and sent to the University of Delaware Soil Testing Lab. The chemical analysis included the following: pH; cation exchange capacity plus exchangeable cations (K, Ca, Mg, Na); total carbon and total nitrogen; particle size analysis; ICP analysis of digestates (Fe, Mn, Al, S, Si); DCB (Dithionite-Citrate-Bicarbonate) extraction for Fe oxides (in progress). Additionally, a subset of samples was

sent to the University of Waterloo for the total, sequential extraction, and methyl Hg analyses (from February sampling). In total, 57 soil core samples were collected and analyzed.

In addition to soil sampling in February, we constructed and installed a series custom-designed multiple redox sensors (PaleoTerra, Netherlands), soil moisture and temperature probes (Decagon, USA). The sensors were placed in the bank soils at RRM 3.5 adjacent to the location of cores (1) and (2) via direct drilling and auguring. (Figures 2, 3). The sensor data has been collected continuously since February 2013 using Campbell and Hypnos dataloggers that were safely stored in a waterproof Pelican case directly at the field site.

In April and May 2013, we installed a series of shallow and deep piezometers next to the soil core locations. Followed by construction, piezometers were developed and equipped with Solinst pressure transducers measuring water level, temperature and conductivity.

In July 2013, we collected and field filtered (0.45 um) water samples from piezometers and stream for the following parameters: MeHg, THg, anions (SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}), dissolved organic carbon (DOC), Fe, Mn, Na, alkalinity, ammonia-N, total P, δ18O and δD. Conductivity, pH, temperature, ORP, DO, S^{2-} and Fe^{2+} were measured directly at the field immediately after sampling.

4. Results

Preliminary soil characteristics and analysis showed the presence of several redox gradient zones in a core (P1) that could be of particular interest for Hg cycling. Particularly, distinctive Fe/Mn(?) oxides/oxyhydroxides were observed in gravel/sand layers between 38.5 and 53.5 in below land surface (BLS) near the active zone of water table fluctuation. Additionally, a pre-colonial wetland soil with the abundant decomposed organic matter was recognized at 53.5 - 58.5 in. Abundant recent plant root material and no buried wetland soil were identified in a soil core (P2). In a contrast to core (P1), the soil core (P2) was not as heterogeneous in terms of redox gradient zones. The concentration of total Hg (sequential extraction summary Hg) in a core (P1) substantially decreased with depth from about 700 mg/kg to 0.1 mg/kg (Figure 4) The highest values were found at top 29 in of the core. Soil samples between 38.5 and 58.5 in contained < 2 mg/kg of Hg. During the field sampling in October 2012, the water table was at about 50 in BLS and depending on seasonal variations it might fluctuate substantially. Therefore this oscillation of water table could impact on redox potential of the system and the mobilization of Hg. The concentration of Hg in a core (P2) was lower compared to core (P1) (up to 244 mg/kg). Figure 6 demonstrates the detailed data on the sequential extraction of Hg analyzed at the University of Waterloo. Overall, a vast majority of Hg exists in the strong complexed (F4) and residual (F5) forms. The analysis for core (P1) showed that only one sample from 53.5-58.5 in BLS (wetland soil) had 58 % of water soluble Hg fraction (F1). About 1% of weak acid extractable Hg fraction (F2) was found in all samples; organo-complexed Hg (F3) increased with depth to up to 82% in sample from 48.5-53.5 in BLS; F4 Hg was the highest between 24 and 43.5 in BLS (up to 61%) and F5 Hg fraction decreased with depth from about 80 % to 5 %. The analysis of core (P2) showed that F5 Hg was the major component in all samples (about 80%) and F4 Hg generally increased with depth (up to 36 %). Particle size analyses showed that soils were dominated by the sand fraction (50-90%) with the variable percentage of silt (1-30%) and clay (2-20%) fractions, respectively (Figure 5).

The analysis of 4 soil cores extracted in February, showed that the concentration of total Hg (wet weight) ranged between 0.04 and 957 mg/kg (core P1A) generally sharply decreasing with depth. The concentration of Hg in core (P5A) was highest between 20 in and 56 in BLS and

reached up to 617 mg/kg (Figure 7). The highest content of Hg correlated well with high values of total soil carbon (TC) (Figure 8). There is a significant correlation between Fe and Mn with the highest values reaching about 20,000 and 460 mg/kg, respectively (Figure 8). The particle size analysis showed that textural class changed from sand to sandy loam and loamy sand.

Our preliminary pilot water sampling of piezometers in July demonstrated that THg ranged from 65 ng/L (pz 1B) to about 523-538 ng/L (pzs 2B and 4B). The concentration of MeHg varied between 7.7 ng/L (pz 2B) to 137 ng/L (pz 3A). THg and MeHg in stream water were 18 ng/L and 0.4 ng/L, respectively (Table 1). The Hg concentration range listed above was lower than expected based on previous work of other research groups that could be due to use of unpreserved sampling methods. Next water sampling is scheduled for the end of September and middle of October to compare the results and Hg dynamics.

5. Key Findings

Our results showed that the concentration of total Hg in soils at RRM 3.5 was up to 900 mg/kg (wet weight).There is a significant redox gradient across the soil profile. Within the top 15-30 in of Hg-rich soil, major changes in redox conditions from oxidizing (Eh ≈+600 mV) to very reducing (Eh ≈-300 mV) followed heavy rainfall and overbank flooding events (Figure 9). Based on the sensor data, the redox responded very quickly to precipitation events allowing us to measure changes in the redox in the unsaturated zone. High variations in stream stage or a prolonged moderate precipitation may govern the surface water - groundwater exchange facilitating the downward or upward movement of the capillary fringe and saturated zone through the soil horizons, affecting soil redox potential, stability of Hg-bearing minerals and leaching of inorganic Hg into dissolved and colloidal phases. These phases may be directly transported to the South River or methylated within the saturated zone of the bank and subsequently released.

6. Next Steps

- Evaluate Hg in groundwater and soil in the context of hydraulics and geochemistry
- Target pre-, post- and storm sampling events this September and October for a next sampling event.
- Correlate the in-situ continuous data set with Hg dynamics in water over base flow and storm sampling.
- Review the groundwater model and assess the potential Hg loading to the river. This data will be compared to the DGT data at the banks (D. Rible group) to help assess whether the Hg in the piezometers actually makes its way into the river.
- Prepare a report of procedures, results, discussion and summary, recommendations for refinements, and presentation to the team.

FIGURES

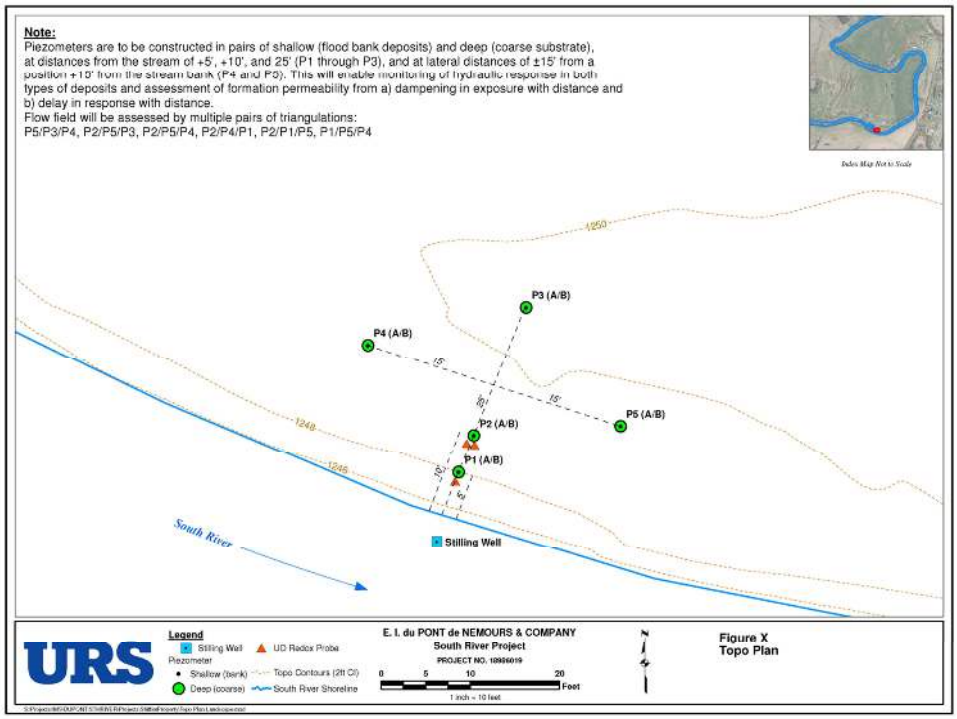

Figure 1: Array of piezometers in combination with redox sensors and soil moisture/temperature probes installed at RRM 3.5

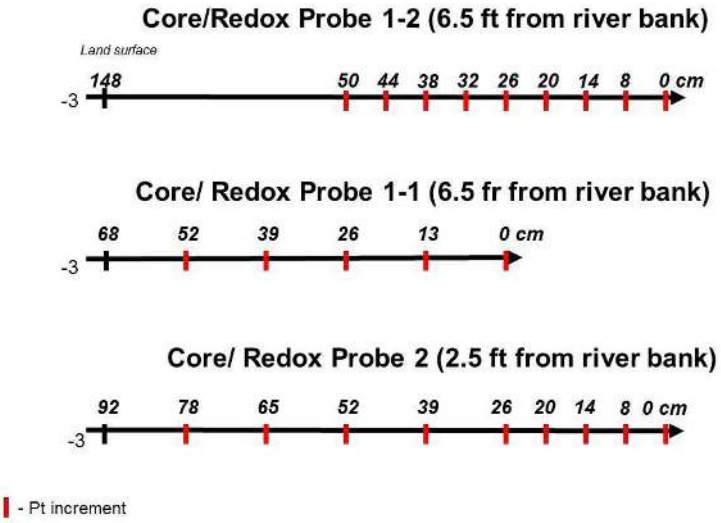

Figure 2: Custom-designed redox probes installed at RRM 3.5

Figure 3: Installation of sensors and datalogging at RRM 3.5

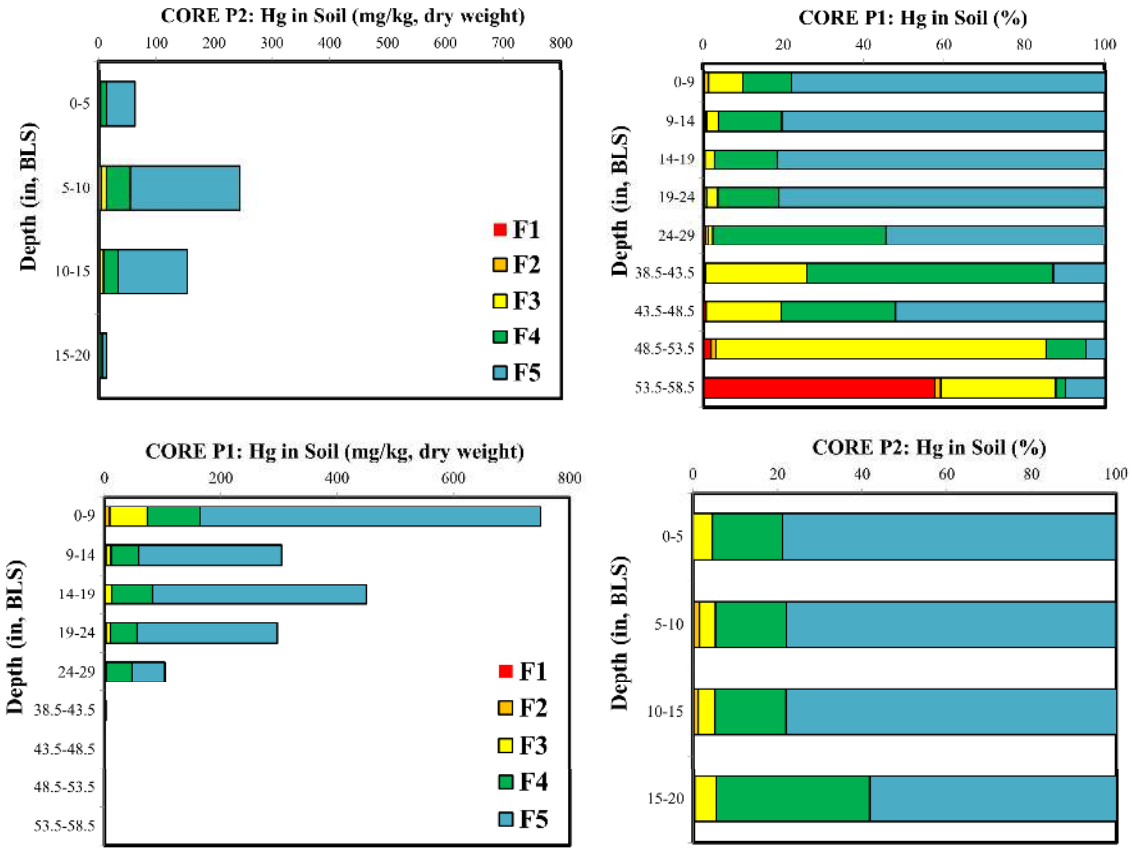

Figure 4: Hg sequential extraction data of soil samples from cores P1and P2 at RRM 3.5 (data from the University of Waterloo). *Note: depth in inches below land surface (BLS); different scales from core P1 to P2; the shift in high percentage of F4 and F5 fractions in core P1between 0-29 in versus 38.5-58.5 in BLS.*

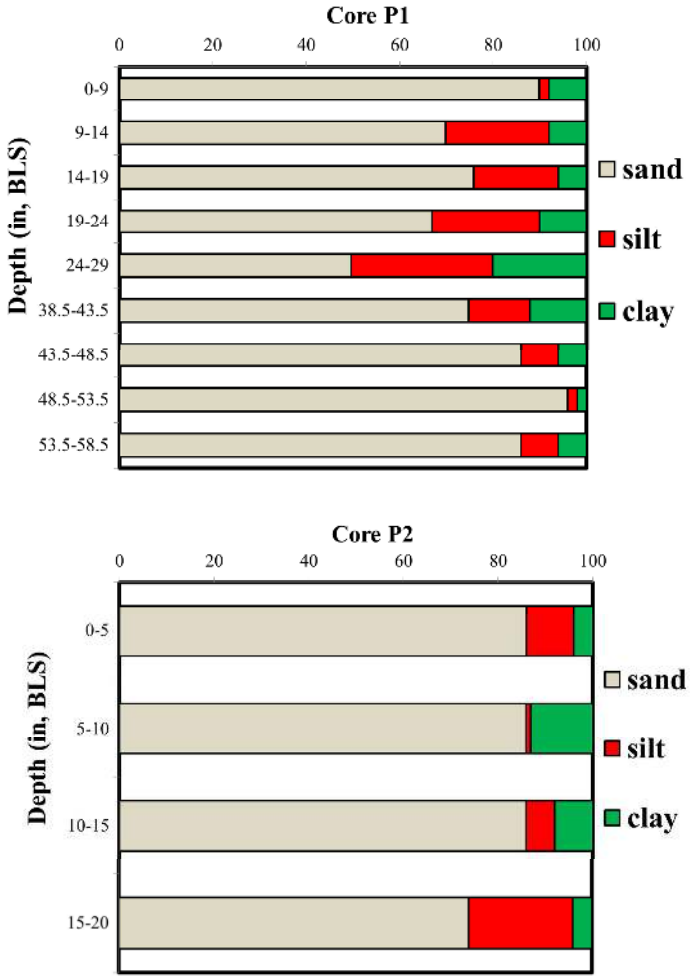

Figure 5: Particle size analysis of soil samples from cores P1 and P2 at RRM 3.5. *Note: depth in inches below land surface (BLS.)*

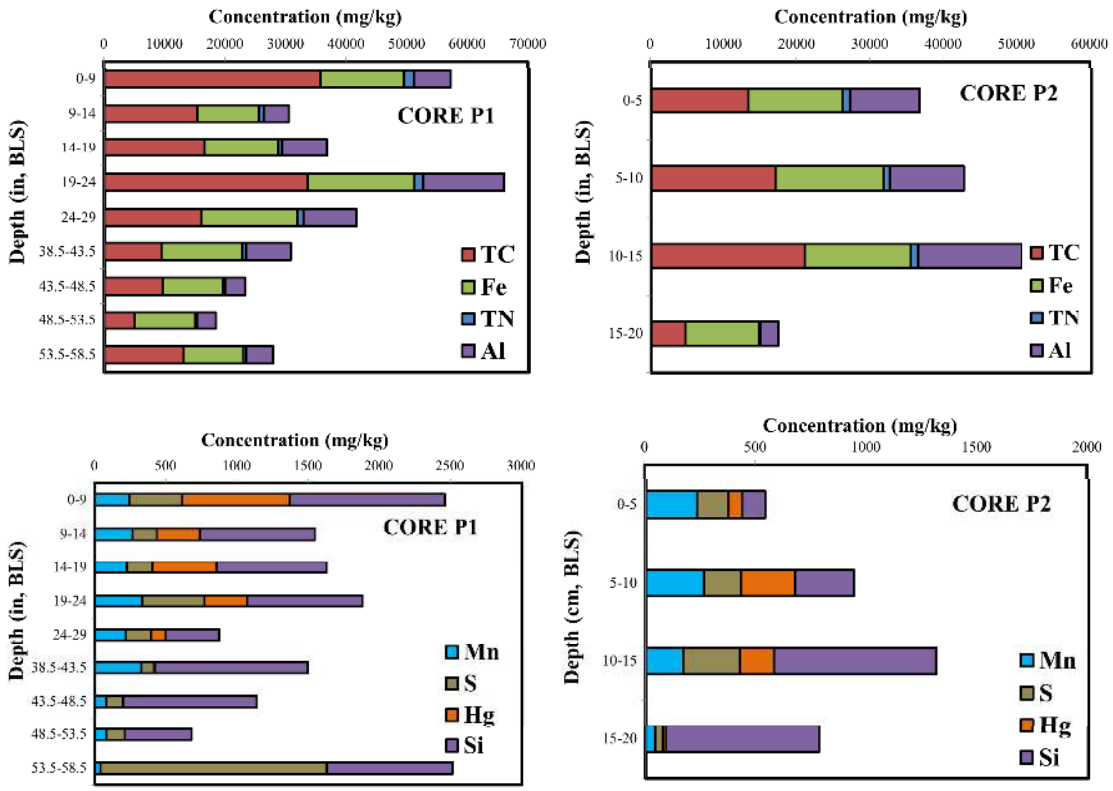

Figure 6: Total Al, Fe, Si, C, N, Hg, S, and Mn for soil samples from cores P1 and P2 at RRM 3.5. *Note: depth in inches below land surface (BLS)*

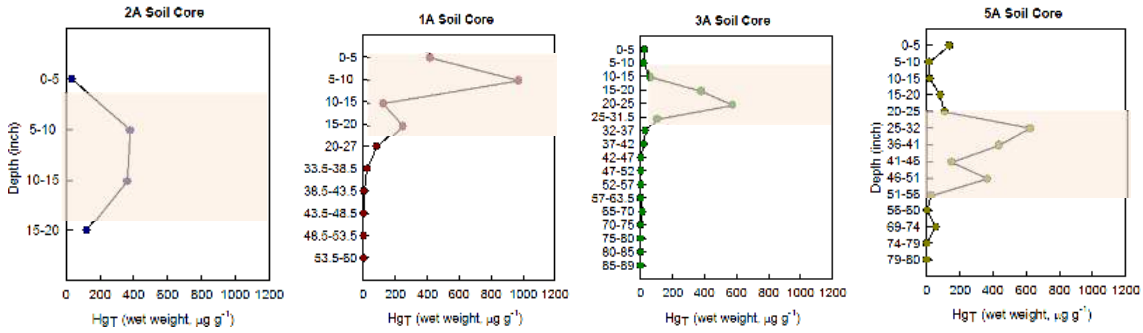

Figure 7: Distribution of total Hg with depth at RRM 3.5 (data from the University of Waterloo)

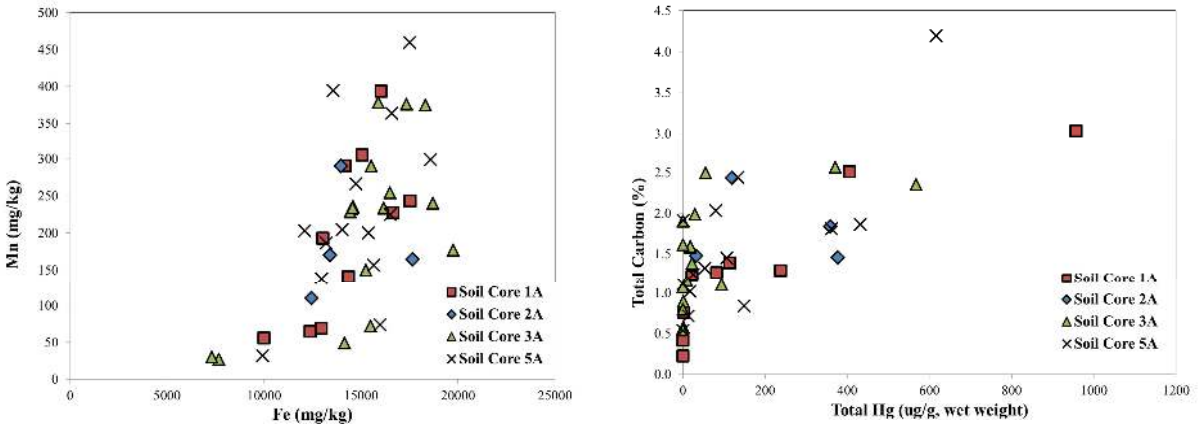

Figure 8: Correlation between Fe vs Mn (left) and TC versus THg (right).

Table 1: THg and MeHg in water samples obtained from piezometers (data from the University of Waterloo).

	July, 2013					August, 2013				
Sample ID	**Sample Preservation**	**Filtration**	**THg (ng L^{-1})**	**MMHg (ng L^{-1})**	**MMHg/THg (%)**	**Sample Preservation**	**Filtration**	**THg (ng L^{-1})**	**MMHg (ng L^{-1})**	**MMHg/THg (%)**
GW0713-RRM-3.5-PZ-1B-Z	Samples are homogenized, seperated into two 60 mL amber vials (one double filtered (0.45 um) and the other is filtered samples as received from the field), and independently acidifiedd and oxidized	Double Filtered 0.45 um	53	27	50	Samples are kept in the sample bottle and are acidified and oxidized as whole				
		0.45 um	73	26	36		0.45 um	65	26	40
GW0713-RRM-3.5-PZ-2B-Z		Double Filtered 0.45 um	85	5.0	6					
		0.45 um	259	7.7	3		0.45 um	538	7.7	1
GW0713-RRM-3.5-PZ-3A-Z		Double Filtered 0.45 um	142	124	87					
		0.45 um	205	137	67		0.45 um	243	137	56
GW0713-RRM-3.5-PZ-3B-Z		Double Filtered 0.45 um	125	57	46					
		0.45 um	165	79	48		0.45 um	217	79	36
GW0713-RRM-3.5-PZ-4B-Z		Double Filtered 0.45 um	54	39	72					
		0.45 um	279	53	19		0.45 um	523	53	10
GW0713-RRM-3.5-PZ-5B-Z		Double Filtered 0.45 um	55	43	79					
		0.45 um	71	52	73		0.45 um	92	52	57
GW0713-RRM-3.5-Z		Double Filtered 0.45 um	6	0.2	4					
		0.45 um	11	0.4	4		0.45 um	18	0.4	2

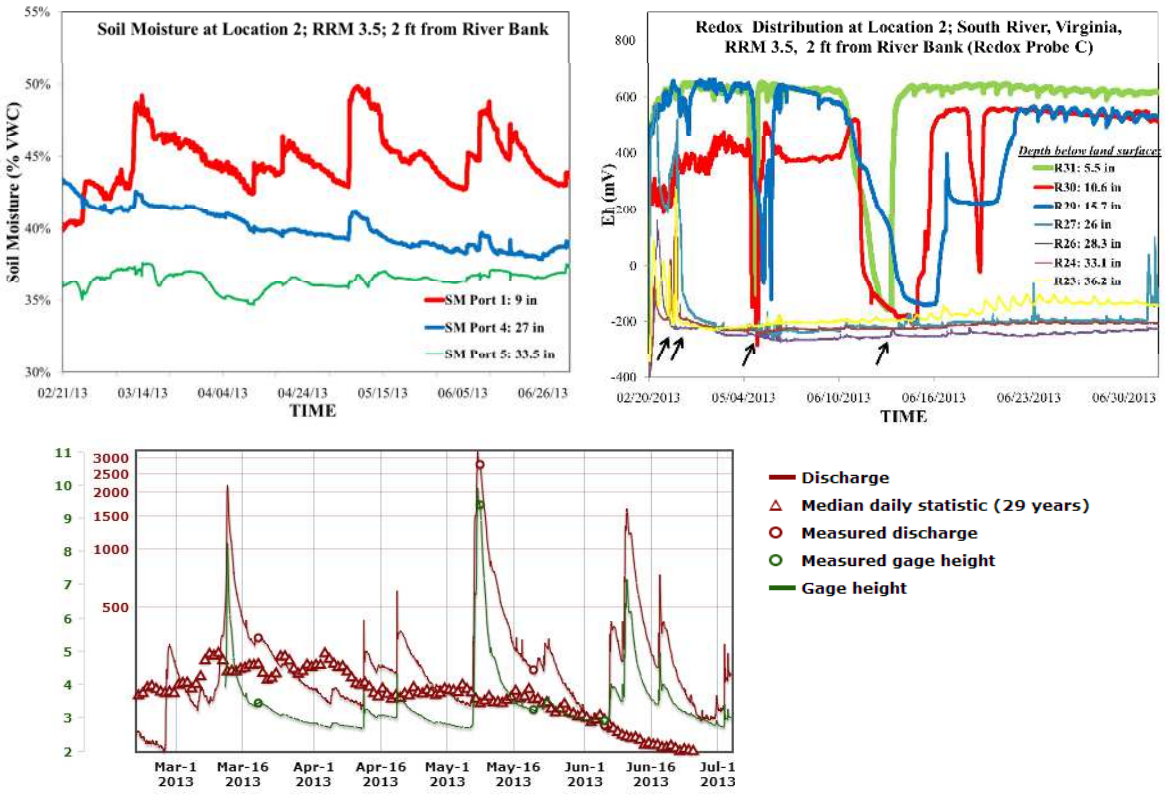

Figure 9: In-situ data for soil moisture (left) and Eh (right) with depth 2ft from the river bank; Discharge and gage height at USGS site 01626850 SOUTH RIVER NEAR DOOMS, VA (bottom). Arrows indicated a dramatic change of redox conditions following heavy rainfall and overbank flooding conditions. *Note: different duration of the redox response to the flooding event in May versus the smaller storm event in June and more sustained redox response. The strong precipitation in May caused drastic and short redox gradient for several days. At the same time, less severe precipitation in June facilitated more sustained response of the redox change, although the redox dropped to the comparative levels. Steady rainfall and slow soil saturation causing the prolonged redox response in June could be more effective in Hg mobilization but this have to be verified with the additional water sampling.*

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