Briefing Paper#4 - Field Measurement of Porewater Hg using DGT and Voltammetry

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The objective of this research task is a better understanding of mercury availability, mobility and methylation in sediments from South River, VA through application of DGT in field sediments. This task is designed to inform the conceptual model of mercury in the river. The ongoing field studies have shown that the diffusion gradient in thin film devices (DGTs) are a very useful tool for in-situ measurement of dissolved and complexed mercury (THg) and methyl mercury (MeHg) in the river and in river sediments. The efforts have been focused on RRM 3.5 and RRM 11.8 as examples of potential source and receiving areas. The sampling has also been conducted in support of a biochar in-situ remediation demonstration in a floodplain pond (Werman Pond). The measurements conducted through summer 2013 have provided three types of information

1. THg and MeHg in porewater in biochar treated and control Wertman pond deposits
2. THg and MeHg in porewater in near shore fine grained and gravel channel deposits
3. THg and MeHg in porewater leaching from bank deposits during declining river hydrographs

Each of these results will be summarized in this briefing paper.

1. THg and MeHg in porewater in biochar treated and control Wertman pond deposits

During the summer of 2011, a biochar amendment (Cowboy© biochar) was placed on the surface of the sediments in a small floodplain pond, Wertman Pond, that is normally isolated from the river. The biochar amendment was placed on the western half of the pond while the eastern portion of the pond was undisturbed as a control. A barrier was placed between the two sides of the pond to ensure biochar and benthos could not move to the control area. DGT sampling via both near surface piston and profiling samplers was conducted in June, August and October of 2011 and in May and August of 2012. Sampling was also planned for May and July 2013 but a high water event in in May 2013 made sampling impossible and may have led to significant exchange across the two sides of the pond as well as disturbance of the pilot demonstration. These factors are under investigation and a further sampling event is planned for October 2013. The discussion herein will focus on the results through August 2012 as shown in Figure 1.

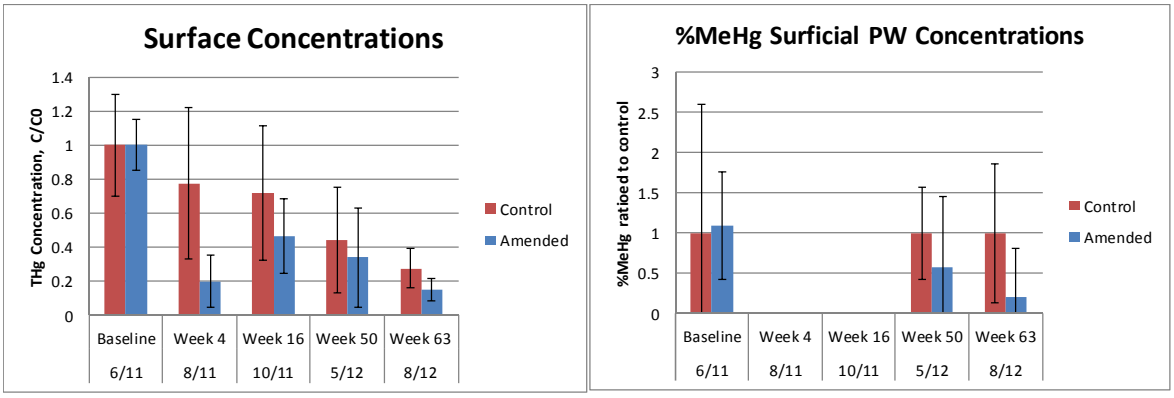

Figure 1 THg and MeHg in near surface porewaters of Wertman Pond

The results in Figure 1 are based upon 3 sample locations sampled in triplicate with a piston sampler. A piston sampler is effectively measuring the porewater in the interval 0-2 cm below the sediment surface. The small number of samples gave rise to substantial variability in the results. The

interpretation of the results were also complicated by the fact that the average porewater concentration in the surficial sediments were initially different in the two sides of the pond before placement of the biochar. As a result the THg concentrations (left hand figure) were normalized to the porewater concentration in the pond sections measured prior to the biochar concentrations. Thus the average normalized concentration during the 6/11 sampling event (prior to biochar placement) is unity. As shown in the figure the placement of biochar led to substantial reductions in THg porewater concentration by 8/11 within two months of placement. There was some evidence a partial rebound over the subsequent year, but porewater concentrations in the amended area remained well below initial porewater concentrations and lower than in the control area throughout the period of sampling. There were also decreases in near surface porewater concentration in the control side over time but the biochar continued to provide a reduction of approximately 50% in THg over the control area.

The ratio of MeHg to THg concentrations provides an indication of the productivity of the sediments relative to methylation. Lower MeHg to THg ratios suggest a lower productivity and methylation rate. The figure on the right hand side shows the ratio of MeHg to THg porewater concentration normalized to the ratio in the control area. By this normalization, the control area ratio is always unity. No MeHg was detectable in August and October 2011, presumably due to low concentrations, particularly in the latter sampling period when water temperatures were such that substantial methylation would not be expected. During periods when MeHg was measurable, the biochar area shows a MeHg to THg ratio of the order of 50% of that in the control area. This suggests that the biochar not only reduced THg by approximately a factor of 2 but also the methylation rate by a factor of 2. Thus the biochar reduced the MeHg by a factor of approximately 4 over that which would have been observed simultaneously in the control area.

The measured reductions in porewater MeHg were approximately consistent with the observed reductions in MeHg in the *Caenis* and *Planorbidae* body burden in the amended areas. Again, the apparent reduction in THg and MeHg in the control area over the sampling period limited the ability to see reductions in the amended area although the amended area body burdens were consistently lower than in the control area. Note that the *Chironomid* data did not show clear trends or reductions as shown by these two species. This may be related to depth of exposure of the various species or other characteristics of their life histories.

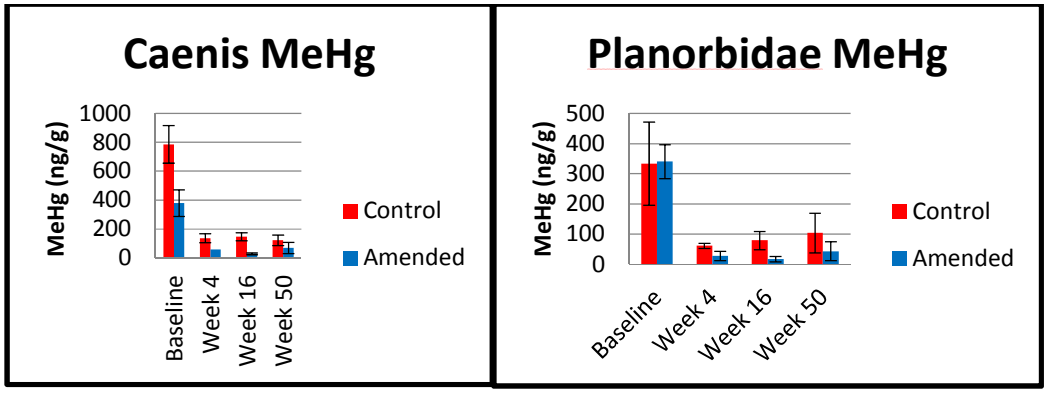

Figure 2 Body burdens of MeHg in two species in Wertman Pond control and biochar amended areas

2. THg and MeHg in porewater in near shore fine grained and gravel channel deposits

Sampling in the fine grained and interbedded gravel deposits in the near shore area employing DGTs was focused on RRM 3.5 and RRM 11.8. RRM 3.5 contains substantial Hg in the bank and river sediments while RRM 11.8 is downstream of the highest Hg concentrations and likely represents recent and ongoing Hg accumulation. The sampling during May of 2013 was during a period of high flow during the drainage portion of the discharge curve after a major storm event. The effects of this on bank deposits is discussed in the next section. Here we focus on porewater concentrations of THg in the near shore fine grained and intermixed gravel deposits that are located 5-10 ft offshore of the bank. Sampling was conducted in these deposits at RRM3.5 and RRM 11.8 in 2010, 2012 and 2013. The degree of intermixed gravel is highly variable in these deposits with more gravel typically found beneath a thin layer of fine grained sediments in relatively quiescent areas near shore and fully intermixed gravel and fine-grained sediment offshore.

Figure 3 compares the 2010 and 2013 porewater concentrations with depth in the two river locations.

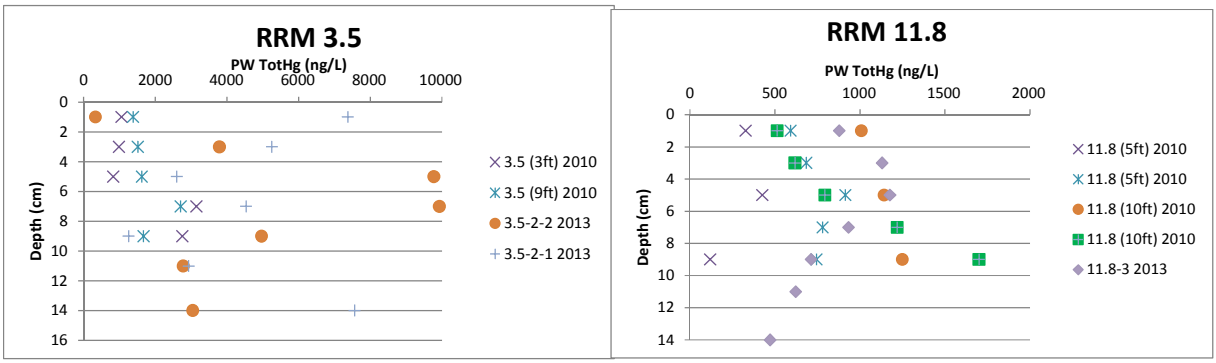

Figure 3 Porewater THg in fine grained near shore channel deposits and intermixed gravel 3-10 ft from bank

Although there are differences between 2010 and 2013, the porewater concentrations are similar in magnitude with average near-surface concentrations of 2,000-5,000 ng/L (2-5 µg/L) at RRM 3.5 and approximately 1,000 ng/L (1µg/L) at RRM 11.8. There are differences in profile shapes, particularly in the suspected source area at RRM 3.5, and these are likely governed by local heterogeneities in sediments, hyporheic exchange and groundwater upwelling. In particular, the high concentrations at 4-8 cm in sample 3.5-2-2 may be associated with local upwelling from the high concentrations noted at the bank at the same time (see section below). Concentrations were lower in 2012 than in either 2010 or 2013 and these are still being investigated. Also under investigation is the flux associated with the measured concentrations. Flow information should allow estimation of the bottom mass transfer coefficient in the stream from which flux, N, can be estimated by

$$N = k_{mt} C_{pw}$$

The mass transfer coefficient, k_{mt}, is typically of the order of 1 cm/hr at the sediment-water interface suggesting that 1000 ng/L in the porewater corresponds to a flux of the order of 1 ng/cm^2/hr. Note that this is a crude estimate that only applies if that concentration occurs at the sediment water interface. The measurements, however, represent an average concentration between 0 and 2 cm and the exchange between this layer and the surface water is likely much less than 1 cm/hr. Further work to quantify the near surface mass transfer coefficient is recommended to improve this estimate.

MeHg concentrations were also similar between 2010 and 2013 in the area offshore from the bank in the fine grained and intermixed gravel deposits as shown in Figure 4. Near surface concentrations of MeHg were 10 ng/L or less at RRM 3.5 and 25 ng/L at RRM 11.8. The profiles suggest that methylation was likely occurring at RRM 3.5 in the deeper more reduced sediments (8 cm or more below the surface). MeHg at RRM 11.8, however, was highest very close to the surface of the sediments, an unlikely location for significant methylation to occur. This would suggest transport (from nearby bank or river sediments or the water column) of MeHg as a mechanisms for the near surface locations at RRM 11.8. The presence at the surface of the sediments would result in benthic exposure to methyl mercury.

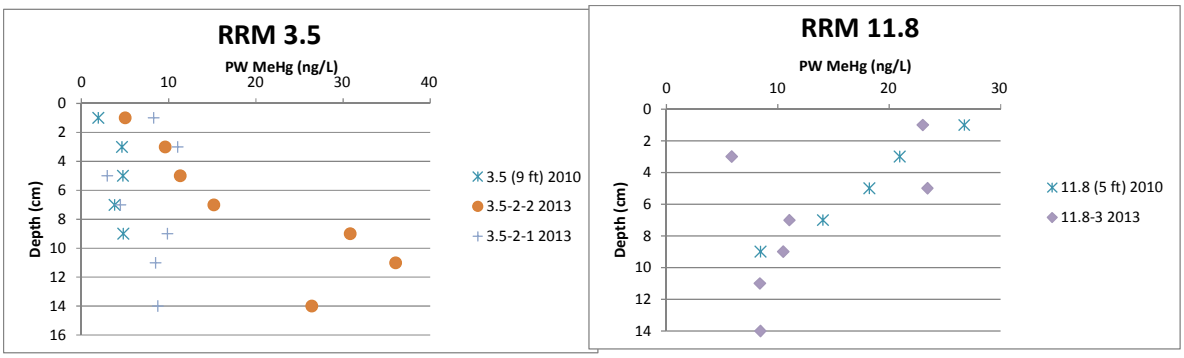

Figure 4 MeHg concentrations in fine grained and intermixed gravel deposits near short in 2010 and 2013

3. THg and MeHg in porewater leaching from bank deposits during declining river hydrographs

During May 2013, sampling was also conducted at the bank-water interface at both RRM 3.5 and RRM 11.8. The sampling also occurred during a rapidly declining water level period after a major storm event. Figure 5 shows the hydrograph in the river before and during the sampling period of May 13-16, 2013. The figure also shows the normal discharge in the river during this period which was a small fraction of the actual flows during sampling. As a result of the high flows and the resulting high water in the river, water levels in the adjacent banks were also high but draining rapidly during the sampling period. DGTs were placed at the bank-water interface to investigate THg and MeHg concentrations in this water.

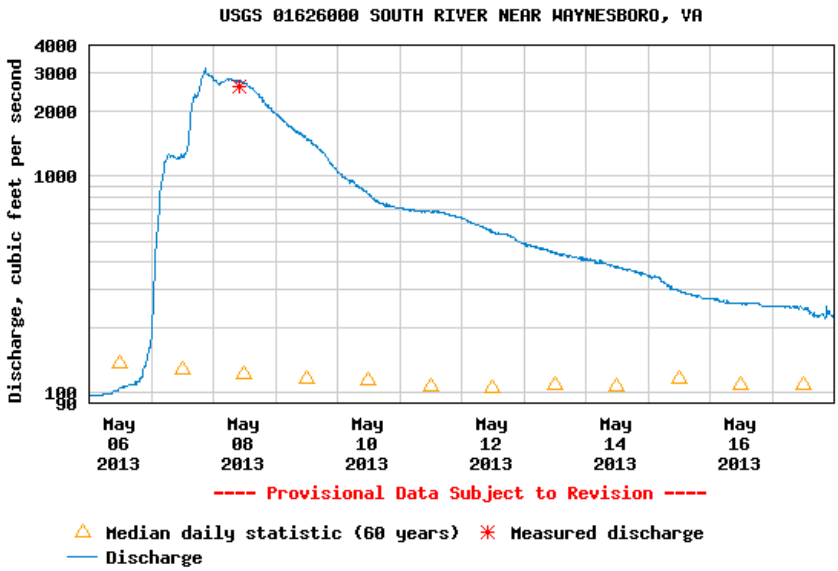

Figure 5 River Hydrograph prior and during sampling event in May 2013

Figure 6 shows measured THg porewater concentrations in samplers at the bank-water interface measured at RRM 3.5 and RRM 11.8 during the sampling event.

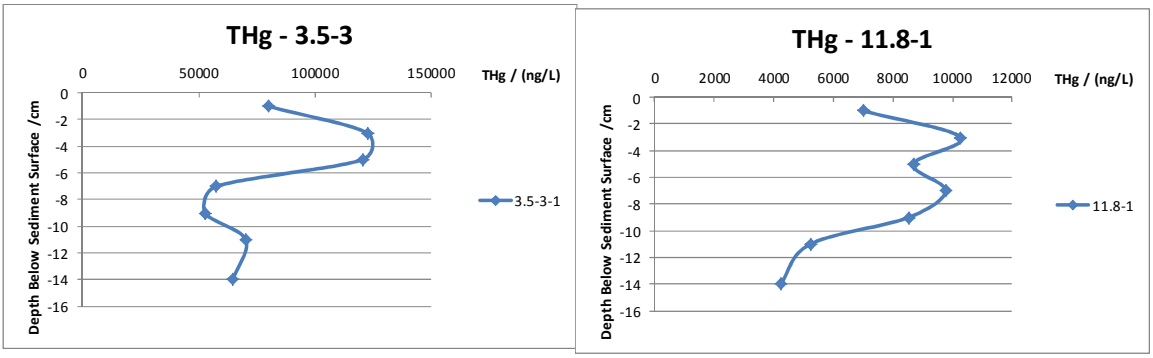

Figure 6 THg concentrations at the bank at RRM 3.5 and 11.8 during a declining hydrograph May 2013

Note that the porewater concentrations at both locations are approximately an order of magnitude higher than detected at near shore locations (Section 2). This suggests that substantial concentrations of THg were released from the bank during the drainage as a result of the declining water levels. These substantially elevated concentrations were noted only within the upper 6-8 cm of the sediments at the bank-water interface where much of the drainage was likely occurring. MeHg concentrations in the same regions, however, were essentially identical to that which was measured in the near shore area as discussed in Section 2. That is, of the order of 10 ng/L MeHg at RRM 3.5 and 20-25 ng/L MeHg at RRM 11.8 were measured at the bank-water interface. The conclusion is that the rapid drainage from the flooded banks during this period released water with high concentrations of THg but conditions for significant methylation of the additional Hg were not present.

Summary

A summary of results-to-date and included below.

- Biochar was observed to provide substantial reductions in porewater THg (factor of approximately 2) and MeHg (factor of approximately 4) over control conditions in Wertman Pond. The effect of the biochar was stronger immediately after placement but had moderated slightly in the year after placement.
- Monitoring is expected to continue at Wertman Pond to identify if these reductions are still observed or if flooding in May 2013 or earlier may have changed pond conditions.
- Monitoring in the near shore fine grained channel deposits and intermixed gravel showed consistent behavior between 2010 and 2013. Near surface sediments (<6-8 cm) showed porewater concentrations of 2000-5000 ng/L THg and 10 ng/L MeHg at RRM 3.5 and around 1000 ng/L THg and 20-30 ng/L MeHg at RRM 11.8.
- The MeHg concentrations at RRM 3.5 suggested methylation in deeper (>8 cm) sediments but at RRM 11.8 peak concentrations were very close to the sediment-water interface which is inconsistent with methylation in fully reduced sediments.
- Sampling at the bank-water interface during a period of significant bank drainage showed substantially elevated THg relative to the near-shore areas although very little difference in MeHg was noted.
- The significance of each of these fluxes relative to the conceptual model of Hg fate and transport is still under investigation.