Briefing Paper – Reactive Capping Assessment, South River VA

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Introduction

Monitoring of the South River by both DGTs and conventional approaches have shown that there is mobile and potentially bioavailable mercury (Hg) leaching from the sediment bed and from bank deposits. The results of DGT monitoring are detailed in a separate briefing paper (DGT Monitoring of THg and MeHg in Porewater, South River VA, Reible et al. 2014). In brief, the results suggest that porewater containing the order of 1 µg/L total mercury (THg) is commonly observed in surficial bed sediments with higher levels, 1-10 µg/L, in particular environments including the near shore of more highly impacted banks such as the HRAD at RRM 3.5. In addition, the DGT measurements suggested that an order of magnitude higher concentration of THg is observed seeping from the base of some banks (specifically the HRAD at RRM 3.5) during transient bank drainage. Methyl mercury (MeHg) in near surface porewaters is typically 0.1-1% of THg, suggestive of marginally productive sediment environment with respect to methylation. During bank drainage, MeHg is typically an order of magnitude lower due to oxic conditions in the drainage. The THg and MeHg release vectors are shown in Figure 1.

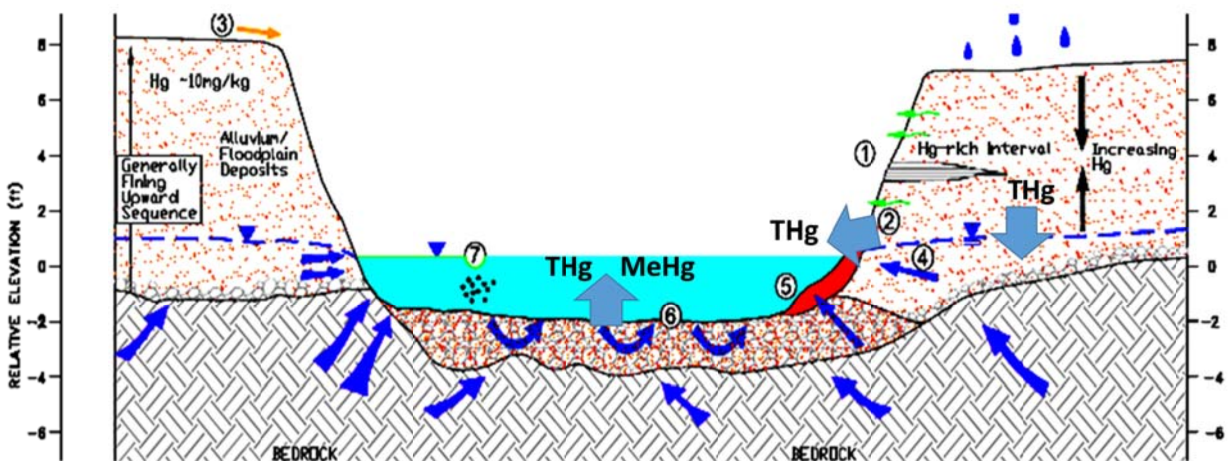

Figure 1 THg and MeHg release vectors in the river

Management of these releases may be possible with sorbing amendments introduced on or in the surface sediments of the river and at the bank. The goal of the project summarized herein is to evaluate potential in-situ capping or treatment options for the South River. The preliminary efforts in this assessment have been directed toward three efforts

1. Baseline studies with benthic organism populated mesocosms with sediment from RRM 11.8.
2. Screening studies of potential sorbing amendments to identify the best choices of amendments for the mesocosm studies.

3. Capping and treatment mesocosm studies with sorbing amendments and conventional caps with sediment from RRM 3.5 to evaluate the performance of potential amendments

Baseline Studies – RRM 11.8

These studies were designed to explore Hg availability and mobility under baseline or unremediated conditions and to evaluate DGTs as a physic-chemical measure of availability by comparing to bioaccumulation in benthic organisms. Mesocosms as depicted in Figure 2 were employed with measurements including profiling voltammetry to assess redox conditions and dynamics and profiling DGTs to measure porewater profiles of THg and MeHg.

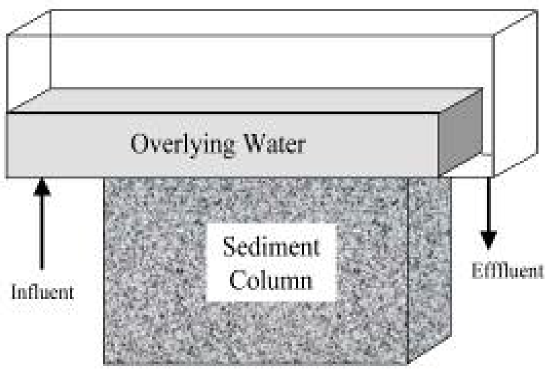

Figure 2 T-cell mesocosms used to evaluate redox dynamics and Hg availability and mobility

A deposit feeding tubificid organism, *Tubifex tubifex*, were introduced to these mesocosms in order to evaluate bioaccumulation and compare to DGT measurements of porewater THg and MeHg. These organisms are not dominant species in the South River ecosystem but are intense sediment mixers through burrowing and conveyor belt feeding and rapidly achieve equilibrium with respect to bioaccumulation. They process 10-20 times their weight in sediment every day by ingesting sediment particles in the organic rich 0.5-10 µm size range. They thus may represent an upper bound to bioaccumulation whereas uptake in other organisms is often less due to slow uptake, insufficient exposure duration, or lack of significant contact with the source substrate (e.g. surface foraging organisms for sediment based contaminants).

Each mesocosm is approximately 120 cm^2 in area and contains sediment about 8 cm deep. The mesocosms were allowed to develop natural redox gradients with a slow overlying water flow over 6-8 weeks before organism introduction. *T. tubifex* was introduced at a density of approximately 25,000/m^2, a typical density of deposit feeding worms in the environment although higher than would be expected in the South River. Voltammetry was used to monitor redox changes in the sediments and DGTs were employed at the end of the experiment to determine porewater concentrations of THg and MeHg. Sediment cores were collected to measure sediment concentration and the entire mesocosm was sacrificed to collect organisms for measurement of bioaccumulation at the end of the 28 day period of exposure.

The bioaccumulation results are shown in Figure 3. The figure shows the bioaccumulation of THg and MeHg in the organism. The organism achieved concentrations approximately 100 times greater than the sediment concentration during the 28 day exposure (after depuration for 24 hours). The bulk of the mass of Hg in the organism was associated with THg which is typical of benthic organisms whereas MeHg is the dominant Hg species in higher order organisms, e.g. fish.

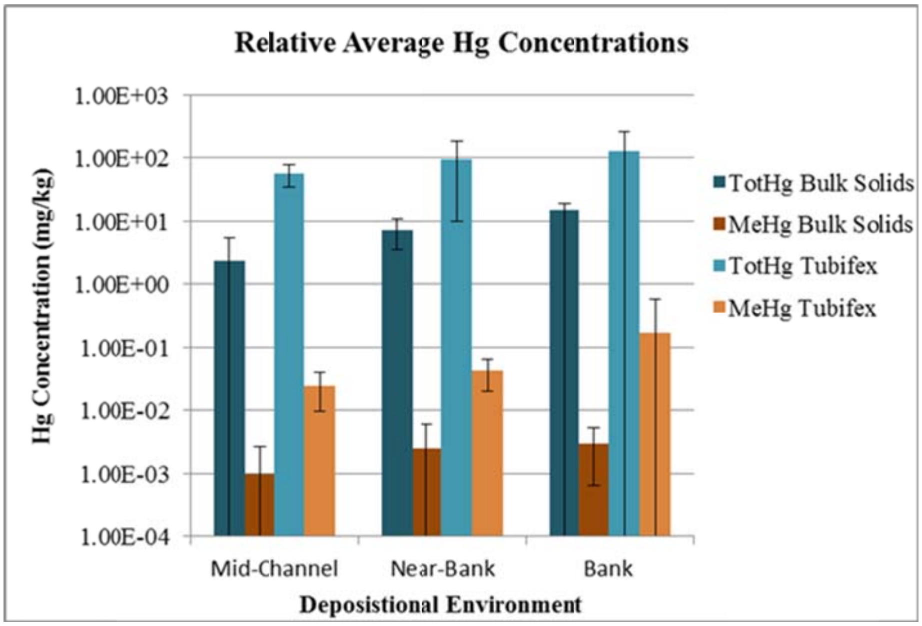

Figure 3 Bioaccumulation of THg and MeHg in T. tubifex after 28 day exposure to the sediments

This bioaccumulation was then correlated with organic carbon normalized bulk solid concentration (as an indicator of the feed to the organisms) and DGT measured THg porewater concentration. The results are shown in Figure 4. The left figure shows a very poor correlation with organic carbon normalized sediment concentration while the right figure shows a weak but better correlation with DGT porewater concentration. This is despite the fact that the fine organic carbon rich sediment is the primary source of food to the organism. A constant biota sediment accumulation factor model of bioaccumulation would presume that there should be a constant slope positive correlation between organic carbon normalized bulk solid Hg concentration and bioaccumulation, which was clearly not observed. Instead, the DGT measured porewater concentration appears to be a better indicator of availability of THg to the organism, despite the fact that the uptake is likely the result of sediment ingestion.

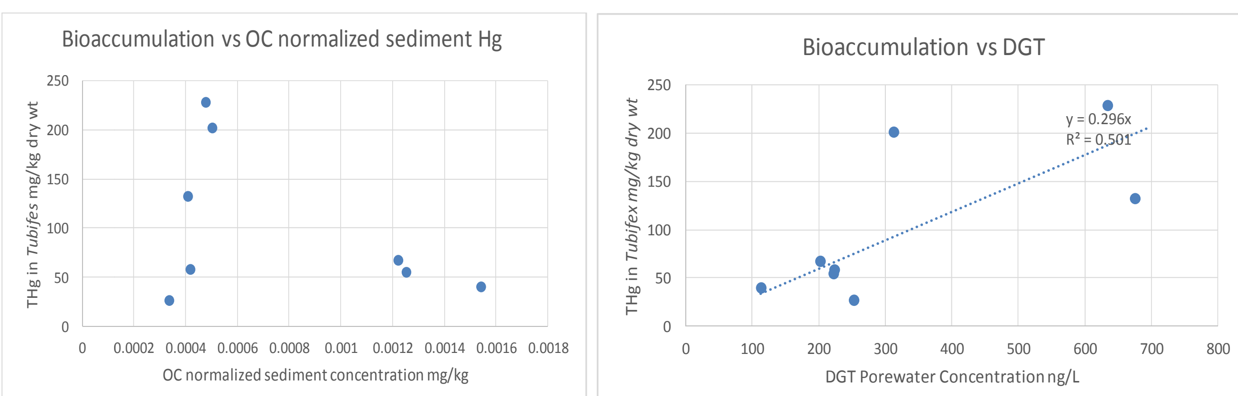

Figure 4 Bioaccumulation vs organic carbon normalized sediment concentration (left) and DGT measured porewater concentration (right). Both measures represent the 0-4 cm average, the approximate depth of organism interactions with the sediment

The DGT-measured porewater concentration profile with depth was also compared to the voltammetry measured redox profile. The results (Figure 5) showed that the porewater concentrations of THg were approximately an order of magnitude higher in the zone where oxygen was detected (shaded area). This is a common observation and is presumably associated with the greater organic carbon oxidation in this layer (increasing natural organic matter, NOM) and the oxidation of low solubility reduced Hg species (e.g. HgS). It is this phenomena that likely leads to the elevated concentrations during drainage from the RRM 3.5 bank (separate briefing paper on DGT monitoring in the river (Reible et al., 2014).

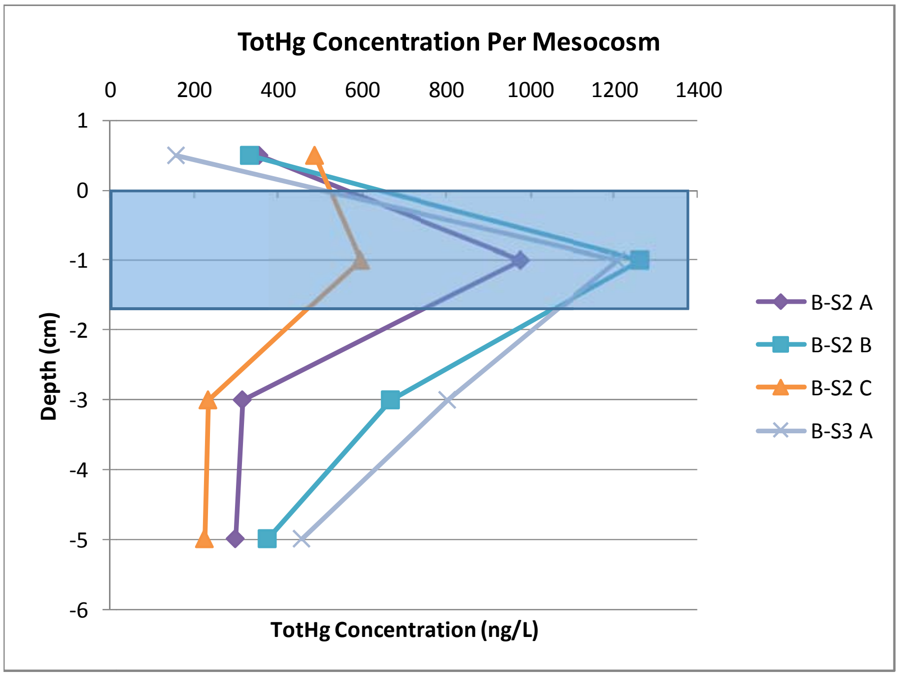

Figure 5 Hg depth profiles showing elevated porewater THg in oxic layer (shaded region)

Sorbing Amendment Studies

Conceptually, we view methylation as the product of desorbed Hg in the porewater, speciation of this Hg into a bioavailable form and finally microbial processes under reducing conditions to give rise to methylation. Amendments can interfere with any of these three steps to reduce methylation. Initial efforts have been focused on reducing the amount of porewater Hg, the first step in this process, by adding a strong sorbent to the sediment or in a cap layer. By attacking Hg availability and mobility, the amount of Hg available for methylation at that location and the amount of Hg that can migrate elsewhere and methylate.

A variety of sorbents were evaluated by conducting sorption studies in freshwater systems. Artificial porewater similar to the river waters was used for these studies due to the lack of large volumes of porewater that could be generated for these studies. The effective partition coefficient of mercury was estimated by measuring the reduction in solution concentration due to the addition of sorbent. The estimated partition coefficients for a variety of sorbents are shown in Table 1.

Table 1 Effective partition coefficients for selected Hg sorbents in freshwater

		Matrix
Material Type	Sorbent	Freshwater
		K_d [L/kg]
Carbon based material	GAC	14300
	Biochar-wood	1310
	Biochar-Rice Husk	190
organophilic clay based materials	PM199 granular	460
Natural materials	Kaolinite	1490
	Sand	6

On the basis of these results, activated carbon and wood-based biochar have been selected for cap amendments in the capping mesocosm studies. Kaolinite has a performance similar to that of biochar but is even more difficult to place than biochar. Organophilic clays were not as effective in this application although this media has proved very effective at other sites, particularly when Hg is primarily associated with NOM. In general, activated carbon has proved the most effective in all conditions and there has been no measurable advantage noted of using sulfur based activated carbons that were primarily developed to treat sulfur containing gas streams.

Capping Mesocosm Studies

The capping mesocosm studies will explore amended caps and in-situ treatments for the South River sediments. The initial studies will focus on near shore and bank sediments from RRM 3.5. Mesocosms like those described above for RRM 11.8 have been set up and redox conditions have been equilibrating. Screening sorption tests (described above) have been conducted to identify appropriate caps for the mesocosm testing. These caps have been tentatively identified as a granular activated carbon cap, a wood-based biochar cap and a conventional sand cap for comparison. A low permeability cap (bentonite in a reactive core mat) will also be evaluated as a tool to control inundation for possible application in leaching bank environments.

The activated carbon and biochar amended caps will be mixed in an approximate loading of 1 lb/ft^2 and mixed throughout a thin (3 cm) sand cap. The mesocosm tests with these and the sand cap will be monitored in the following ways

- Voltammetry to monitor changes in redox conditions after cap placement
- Overlying water measurements before and after cap placement to demonstrate flux reduction
- DGT profiling of porewater THg and MeHg concentration to evaluate response of these parameters in the underlying sediment as well as any migration over time into the overlying cap

Initial efforts (to be completed by Jan 2015) will be focused on static cap conditions similar to those observed on the river bottom. Subsequent experiments in 2015 will be focused on the dynamic environment typical of the banks wetting, drying cycles and the performance of the low permeability cap layer as well as the amended caps to manage the resulting bank leaching.