Briefing Paper – DGT Monitoring of THg and MeHg in Porewater, South River VA

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Assessing Hg speciation taken up by DGT

The monitoring undertaken by the Reible group has focused on using diffusion gradient in thin film (DGT) devices to measure total mercury (THg) and methyl mercury (MeHg). These devices accumulate THg and MeHg onto a sorbing thiol-resin separated from the surrounding medium by a thin diffusion layer. The rate of uptake is dependent upon the rate of diffusion through this layer and the concentration of the species in the porespace of the surrounding medium. THg is generally associated with porewater ions including chloride and sulfides, dissolved organic matter or suspended particulate matter rather than freely dissolved. Work has been undertaken during 2014 to better understand which of these species pass the diffusion layer and are therefore measured by the DGT. It is believed that the biologically relevant mercury species are those that readily pass a cell wall and therefore potentially limited to molecular and nanometer sized complexes. The purpose of the DGT is to measure THg in these species rather than 100-450 nm colloidal and particulate associated Hg which would still be expected to pass a 0.45 μm filter that operational defines "dissolved Hg" by conventional water and porewater sampling. We undertook various experiments to demonstrate the ability of the DGT device to reject Hg associated with larger particles and to evaluate the uptake of Hg associated with dissolved organic matter.

The results of the studies are summarized in the two figures below. In the first, thiol resins of two particle sizes, 60 μm and 0.2 μm (200 nm), were used to evaluate particle rejection by the DGT gel. The Hg was expected to be strongly associated with these resins and if these particles are rejected by the diffusion gel, little or no Hg should be taken up by the DGT when exposed to aqueous solutions of these resins. This was observed with significant uptake from Hg in the absence of particles and essentially no detectable uptake (background uptake) in the presence of Hg associated with the 60 and 0.2 μm particles. Aggregation was noted with the 0.2 μm particles which may limit the ability to categorically state that a 0.2 μm does not pass the diffusion layer, but no evidence of uptake of particulate bound Hg was noted.

In the second of the two figures, Hg was exposed to different size fractions of natural organic matter (NOM) in aqueous solutions. The NOM solutions were prepared by wetting Suwanee River NOM and different size fractions were produced by sequential ultrafiltration. The largest size fraction would be expected to be of the order of 10 nm in size. Very little difference between uptake from solutions with no NOM and uptake with different NOM sizes was noted. This may also reflect the difficulties of separating the NOM due to NOM aggregation during ultrafiltration (i.e. small molecular weight NOM may have been retained on high molecular weight filters) or weak binding between Hg and the NOM. If NOM was not migrating through the DGT, however, a more significant reduction in Hg uptake would have been expected.

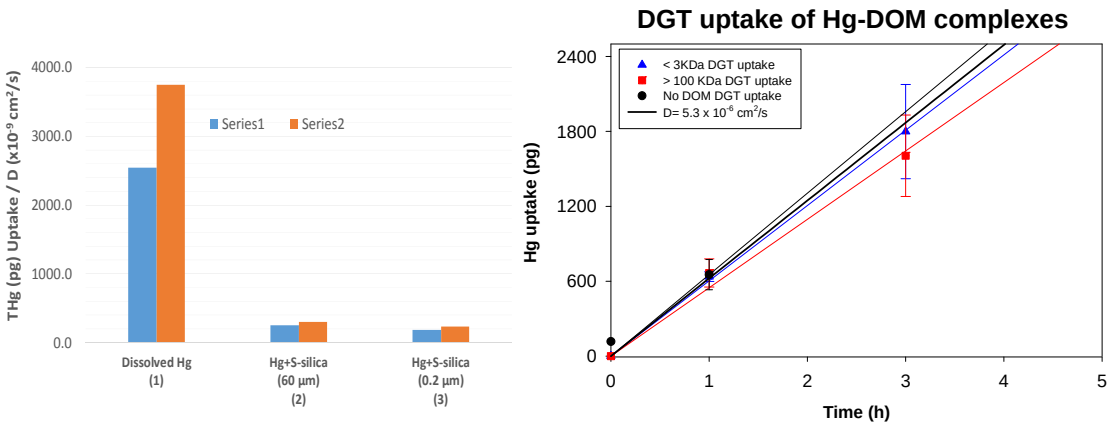

Figure 1 (a) Uptake from dissolved and particulate bound Hg and (b) uptake over time of dissolved and DOM associated Hg

As a result of the two experiments and other supporting information, it is believed that only freely associated Hg and Hg associated with molecular sized complexes (<10 nm) are believed to be taken up by the DGT. The DGT appears to successfully reject particulate bound Hg associated with colloidal particles that might pass a conventional filtration with 0.45 µm filters. This is consistent with the work of Fatin-Rouge et al. (2004) who demonstrated that aqueous agarose gels similar to that used for the diffusion layer do not allow appreciable diffusion of particles larger than around 50 nm.[1]

As a result of the apparent rejection of particulate bound Hg, it is believed that the DGT provides a better indication of bioavailable Hg than filtered porewater samples. Hg associated with particles larger than 100 nm are unlikely to be biological relevant, at least by passive cell uptake processes. Preliminary experiments have in fact shown that the DGTs provide a better correlation with bioaccumulation in deposit feeding organisms than organic carbon normalized solid Hg concentration (see separate briefing paper Reactive Cap Assessment, South River, VA, Reible et al., 2014)

Summary of DGT monitoring in South River

DGT porewater measurements of THg and MeHg have been conducted since 2010. Monitoring has focused in surficial sediments at RRM 0.1, RRM 3.5 and RRM 11.8. Typically monitoring with both piston (approximately 0-2 cm) and depth profiling (0-10 cm) DGTs was conducted at locations near the bank (2-5 ft from the bank), in transitional sediments (5-15 ft from shore) and channel sediments (>15 ft from shore). At RRM 11.8, the near shore sediments were fine grained channel margin deposits while increasing coarse sand and gravel deposits were noted as you moved offshore. A similar trend was noted at RRM 3.5 although substantial amounts of sand and gravel was found at all sampling locations at that station. Fine sands were noted at RRM 0.1 at all sampling locations, likely the result of deposition from the adjacent runoff channel. Additional sampling was conducted at the bank-water interface at RRM 3.5 and 11.8 in 2013 and 2014 and at RRM 0.1 at the bank stabilization pilot in 2014.

Typical concentrations of THg as a function of depth at RRM 3.5 (left) and 11.8 (right) are shown in Figure 2. At RRM 11.8 peak concentrations were generally of the order of 1000 ng/L (ppt) or 1 µg/L of THg. At RRM 3.5 similar concentrations of THg were noted offshore in sand and gravel deposits but near the bank in this HRAD area, elevated THg concentrations were noted in the range of 1000-10,000 ng/L

[1] Fatin-Rouge et al., Biophysical Journal, 2004

or 1-10 µg/L. Sampling until 2010 was entirely during low river stage and flows (100-300 ft^3/sec) and the concentrations in Figure 2 are associated with these baseline flow conditions. In 2014, peepers were used as an independent measure of THg in porewater and also showed 1000-10,000 ng/L at the base of RRM 3.5 bank during these baseline flow conditions and serve as a confirmation of the DGT measurements.

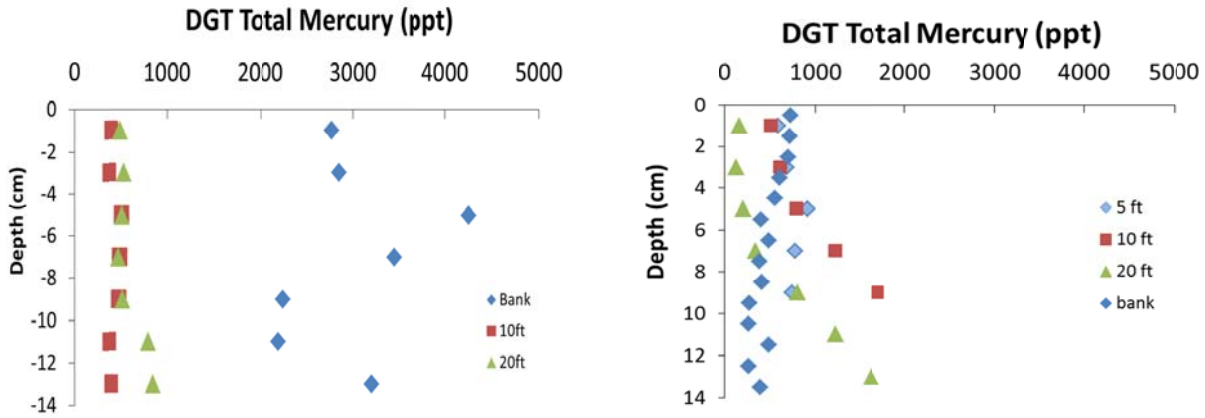

Figure 2 (a) THg in porewater under baseline flow conditions at RRM 43.5 and (b) THg in porewater under baseline flow conditions at RRM 11.8

MeHg concentrations in the near surface sediments under baseline conditions were typically 1-10 ng/L although 10-100 ng/L MeHg was noted in the fine grained channel margin deposits at RRM 11.8 and 50-300 ng/L was noted in the bank and near shore areas of RRM 3.5. The MeHg levels were typically less than 1% of the THg measured in the porewater at the same location which suggests that the system is not very productive relative to methylation. Typically, highly methylating sediments (e.g. organic rich salt marshes) exhibit porewater MeHg to THg levels of >10% (1-10% bulk solid basis).

In May 2013, sampling coincided with a declining stage after a storm related high flow event in the river. Peak river flows immediately before the beginning of sampling were in excess of 3000 ft^3/sec and declined during the 2 day sampling period to about 1000 ft^3/sec. THg concentrations in the riverbed and at the bank at RRM 11.9 were similar to that under baseline flow conditions. THg concentrations at the base of the bank at RRM 3.5, however, were significantly increased with peak concentrations of nearly 200, 000 ng/L or 200 µg/L. During May of 2014, sampling was conducted both immediately before a storm event and during the declining stage after a storm event as shown in Figure 3.

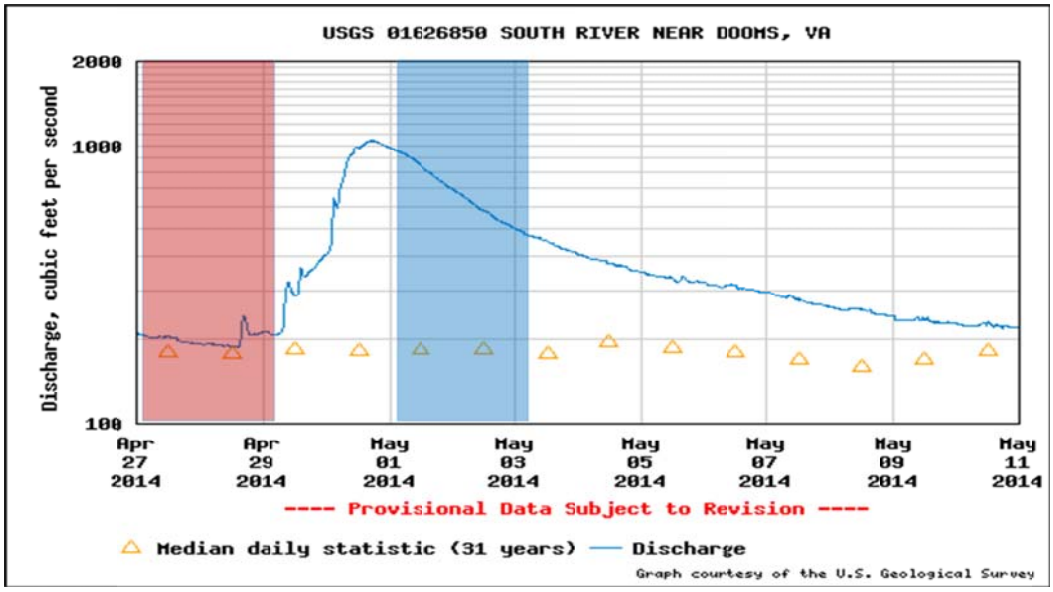

Figure 3 Sampling periods (shaded) and river hydrograph at Dooms, VA

The THg porewater concentration at the base of the bank during these two periods is shown in Figure 4 with the left hand figure showing typical baseline flow concentrations of <10, 000 ng/L (<10 µg/L) THg and an order of magnitude higher concentrations at the same locations a few days later during the declining stage conditions.

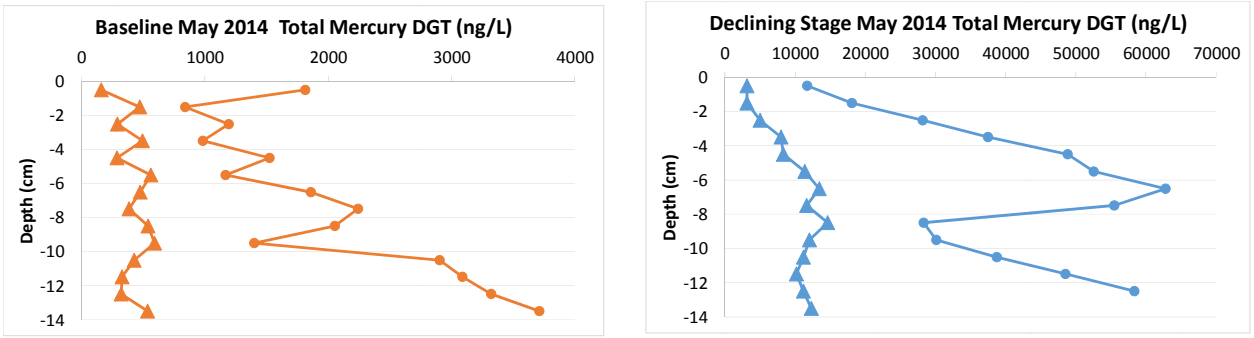

Figure 4 THg porewater concentration during the baseline (left) and decling stage (right) conditions of May 2014

The likely mechanism for this phenomena is the rapid rise of water into the RRM 3.5 bank sediments during periods of high water, wetting zones that had previously been unsaturated and oxic. Oxic conditions leads to reduced amounts of THg in low solubility reduced phases and also typically leads to higher amounts of DOM due to great degradation of organic carbon. Both of these lead to the observation of greater amounts of THg in porewater per unit concentration in the bulk solids in oxic environments (i.e. a lower effective Hg partition coefficient). Once this area is inundated and begins to drain, the water returning to the river contains these elevated levels of THg. This is depicted in Figure 5. THg is released into the draining water and that water either returns to the river at the base of the bank or moves vertically down where it is diluted by the relatively rapid flushing of water in the sand-gravel zone at the base of the bank. Regardless of the flow movement, however, the THg released into the inundation water is carried into the river as the bank drains. The sampling wells in the bank soils at RRM 3.5 are believed to be largely connected to the relatively well flushed zone at the base of the bank

and this was borne out by simultaneous measurements of THg in the wells and in DGTs placed in the wells. These measurements were similar to each other but showed <100 ng/L THg compared to the >10,000 ng/L at the undiluted face of the bank. Well concentrations may also be lower than the seepage face as a result of lower soil Hg concentrations at those locations in the bank and thus lower concentrations in the draining water.

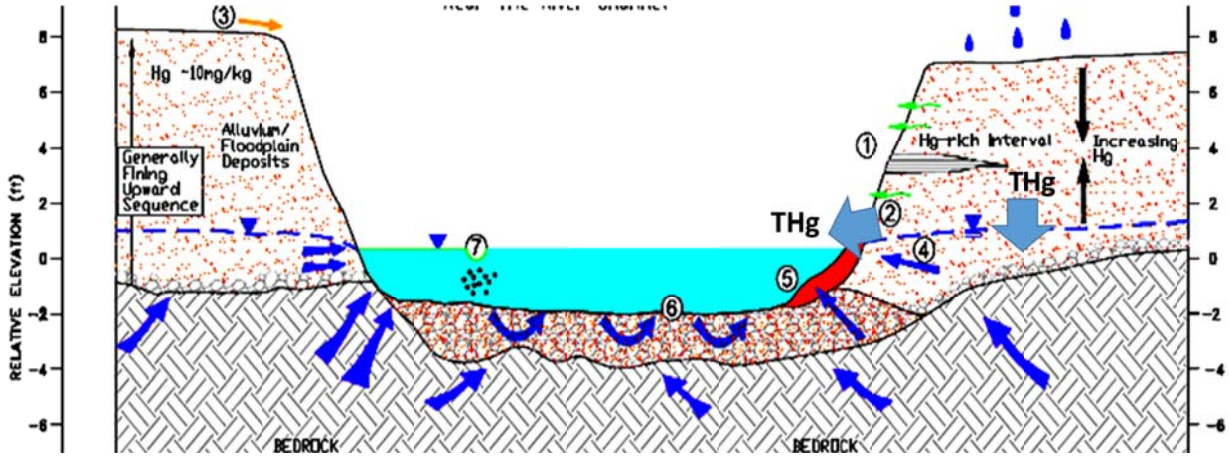

Figure 5 Conceptual model of THg release during bank drainage

During May 2014, the river stage during the storm event and presumably the resulting inundation of the bank, was approximately half as much as during the May 2013 monitoring event. As a result, the concentrations of THg in the bank seepage face peaked at approximately 60,000 ng/L (60 µg/L) during May 2014 compared to almost 200,000 ng/L (200 µg/L) during May 2013. This remains an order of magnitude higher than the typical 1-10 µg/L during baseline flow conditions.

Methyl mercury concentrations were also monitored at the base of the bank and are typically an order of magnitude *lower* during the bank drainage period. This is consistent with the conceptual model that the elevated THg is associated with drainage of oxic water from the bank and also consistent with voltammetry measurements at the bank-water interface that shows that oxygen is near saturation at all depths during the drainage cycle. These conditions would limit any methylation. During the baseline flows oxygen is observed in only the upper 1-2 cm at the bank-water interface and there is evidence of reduction deeper in the profile, leading to greater amounts of methylation.

Significant storm events followed by inundation and then drainage of the banks occur of the order of once per month in the South River and more often during certain times of the year. It is not known if there are other areas of the river giving rise to elevated THg releases during drainage cycles. During July 2014, additional DGT sampling was conducted at the bank stabilization pilot at RRM 0.1 and showed that at least during baseline flow conditions the concentrations of THg at the base of the bank are substantially lower (168 ng/L) than at RRM 3.5. Additional sampling should be conducted at the base of the stabilization pilot and at other potential HRAD locations during drainage cycles to assess the significance of this mechanism on mercury loading in the river. If this mechanism leads to substantial mercury loading elsewhere in the river, it may be appropriate to consider leachate control as part of the bank stabilization efforts. Potential approaches to manage leachate are under investigation in the reactive capping assessment (see separate briefing paper, Reactive Cap Assessment, South River, VA, Reible et al., 2014).