

# Mercury Bioaccumulation from Unamended and Amended South River Sediments – September 2014 Update

M.C. Newman - VIMS

## Background

As the DuPont team moves into the remediation stage for the South River, sediment amendment with sorbents has emerged as one promising tool. Candidate materials range from expensive thiol SAMM<sup>®</sup> nanoparticles, to fabricated iron sulfide nanoparticles, to Exponent's moderately priced Sedimite<sup>®</sup>, to low-cost biochars. The ongoing Wertman pond amendment trial and results from the VIMS 2013 study indicate that Cowboy<sup>®</sup> biochar is a viable candidate for final remediation activities. A previous South River study (Bundschuh et al. 2011)<sup>1</sup> and the assays from the VIMS 2013 study suggested that Sedimite<sup>®</sup> might have the drawback of reducing detrital processing in the detritivory-dominated South River.

The VIMS 2013 study documented general shifts in both bioaccumulation and detrital processing at 0, 1.5, 3, and 6 months after sorbent mixing with Dooms Crossing sediment. Bioaccumulation was significant after 10 days of exposure to sediments but sediment amending did reduce the degree of bioaccumulation. The influence of sediment-amendment mixture ageing on efficacy was not definitive at the end of 2013 study although there did seem to be a decrease in efficacy with time. Explicit bioaccumulation modeling and relative bioavailability estimation were needed to clearly define any remediation-associated bioaccumulation reduction.

The freshwater amphipod, *Hyalella azteca*, was selected as the model collector/shredder for the VIMS studies because it is a common North American collector/shredder, is used widely for ecotoxicological studies, and was used successfully by the VIMS team for an initial study of South River remediation with Sedimite<sup>®</sup> (Bundschuh et al. 2011). It represents the epibenthic invertebrate guild that dominates the base of the South River food web. It is amenable to field exposures in small screened enclosures so that it can potentially be used for future *in situ* post-remediation studies.

## Specific 2014 Objectives

1. To model mercury bioaccumulation from contaminated sediments<sup>2</sup>, determining the decrease in bioavailability of mercury in sediments amended with Sedimite<sup>®</sup>, or one of three size-grades of Cowboy<sup>®</sup> biochar (<0.25mm, 0.25-1mm, and 1-2mm sieved). Bioavailability is estimated relative to that of unamended sediment.
2. To model mercury bioaccumulation and estimate relative bioavailability from sediments 0, 2 and 4 months after amendment of the sediment. The intent is to document any decrease in efficacy with time.

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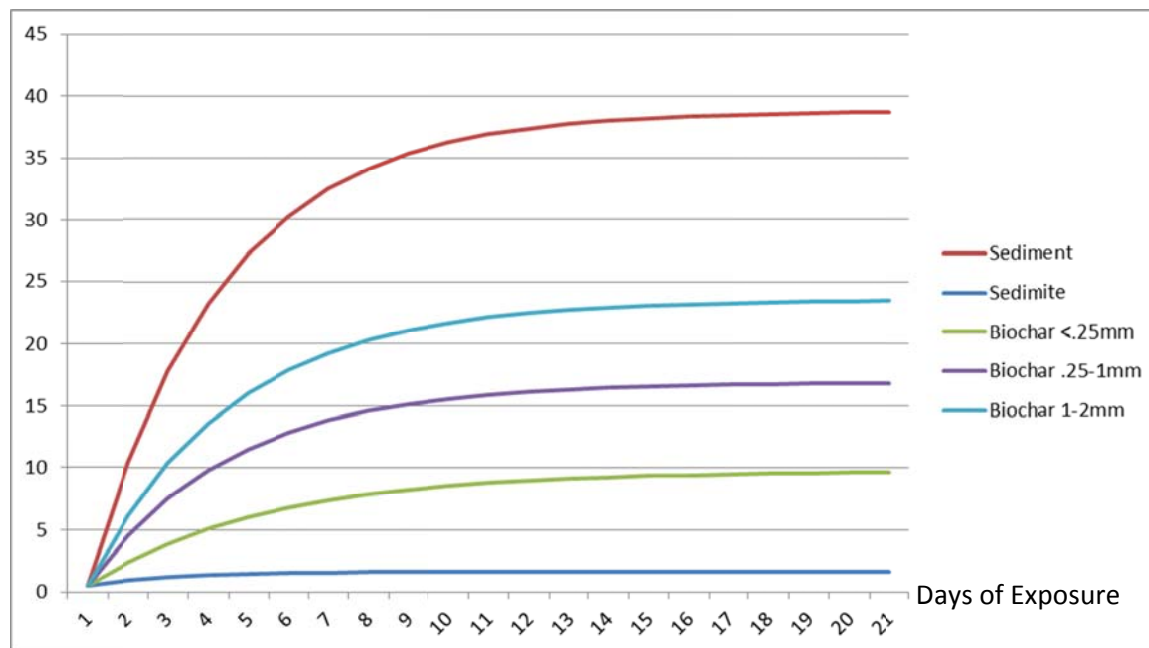
<sup>1</sup> Arch. Environ. Contam. Toxicol. 60: 437.

<sup>2</sup> Sediments used in these 2014 assays were collected by Scott Gregory and Richard Landis at the Augusta Forestry Center during the spring of 2014. The mean total mercury in this sediment was 13.7 ug/g DW (SD = 4.7, n = 20). Organic matter, measured as percentage weight loss on ignition, averaged 8.3% (SD = 1.6%, n = 5).

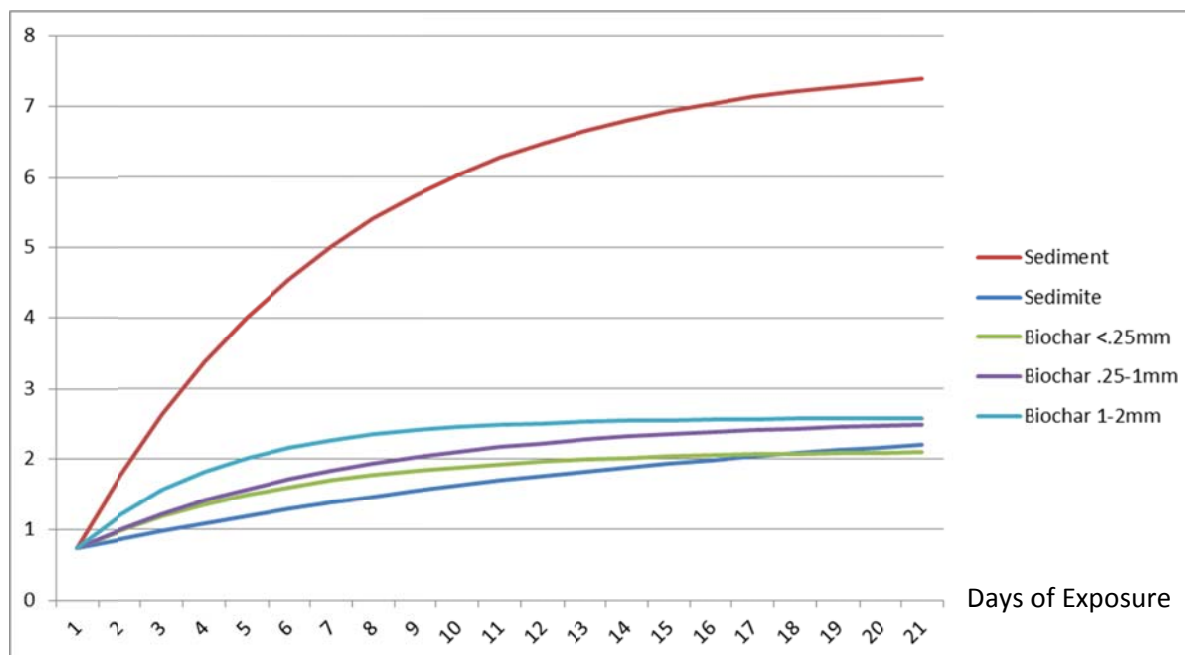
## Preliminary 2014 Results

This study estimates mercury bioaccumulation from amended sediments from South River and compares that bioaccumulation to that of unamended sediment. Sediment amended with Sedimite<sup>®</sup> or one of several size classes of Cowboy<sup>®</sup> biochar were studied. Cowboy<sup>®</sup> biochar treatments involved biochar sieved into three size classes: <0.25, 0.25-1, and 1-2 mm. Amending was done at 0.1 gm of material per gm of dried sediment. Treatments were established and the bioaccumulation quantified over 20 day periods immediately, 2, and 4 months after blending. Each treatment was done in duplicate during each period with 100 amphipods per replicate. Two assays are complete at this time and a final one (4 months) is underway. The bioaccumulation of total mercury in amphipods was measured during each time course (0, 1, 2, 3, 4, 5, 7, 9, 12, 15, 20 days) and fit to the following model by nonlinear regression (SAS program),

where  $[Hg]_t$  = concentration in amphipods at time,  $t$ ,  $[Hg]_{source}$  = mercury concentration in source sediment,  $[Hg]_0$  = mercury in amphipods at time 0,  $k_e$  = elimination rate constant, and  $k_u$  = uptake clearance rate. The results are presented below as the predicted whole body concentration after 20 days exposure. The concentration at 20 days reflects the concentration at practical equilibrium, i.e., the predicted 95% equilibrium concentration.



**Figure 1.** Assay 1 started immediately after blending the sediment and amendments. Relative bioavailability (%) is estimated as 100 times the predicted concentration at 20 days divided by the same for the sediment-only treatment. 38.8 mg/kg is the predicted Hg concentration of amphipods after 20 days exposure to untreated sediment (13.7 mg Hg/kg DW, red line). This assay was conducted in a dark, constant temperature incubator (Mean Temperature = 23.3 C, SD = 0.1 C, n = 41). An initial sample of amphipods used in the assay produced a mean amphipod dry weight of 0.35 mg (SD = 0.11 mg, n = 31). Replicate (n = 45) analyses of the DORM 3 standard material were used to estimate mercury analysis accuracy (percent recovery = 99.7%) and precision (RSD = 3.0%).



**Figure 2.** Assay 2 conducted two months after blending the sediment and amendments. Relative bioavailability is expressed as a percentage of the availability from the untreated sediment (red line). This assay was conducted in a dark, constant temperature incubator (Mean Temperature = 23.3 C, SD = 0.1 C, n = 40). An initial sample of amphipods used in the assay produced a mean amphipod dry weight of 0.33 mg (SD = 0.13 mg, n = 40). Replicate (n = 42) analyses of the DORM 3 standard material were used to estimate mercury analysis accuracy (percent recovery = 99.0%) and precision (RSD = 2.4%).

### Summary of Results To-date

The mercury from the Dooms sediments was more readily available to amphipods initially than 2 months post-blending. Initially the Sedimite<sup>®</sup> was the most effective sorbent and smaller diameter Cowboy<sup>®</sup> biochar granules were more effective than larger diameter biochar granules. After 2 months, the mercury in the sediments was less bioavailable and all sorbent materials substantially reduced its bioavailability during the assay, i.e, 23 to 35% as bioavailable as that in unamended sediment.

### Next Steps

The third (4 months) assay will be completed in November, achieving the two 2014 objectives. To find a possible explanation for the substantial changes in bioavailability in the unamended sediments through time, samples of sediments from the three assays will be sent to CEBAM for methylmercury analysis. Also, samples of the sorbent materials are being analyzed for available surface area so that differences among materials can be explored relative to differences in surface areas of the four materials.

The promise of successful remediation by biochar amendment is apparent from these results. What remains to be done is to move the investigations into the field. Leaf pack deployment to measure detrital processing (to establish a baseline prior to any amendment activities) and also mesocosms to quantify bioaccumulation and detrital processing differences upon field treatment seem very appropriate at this time.