

# **Evaluation of Potential Treatment Methods for Mercury-Bearing Riverbank Sediments and Soils from the South River, Virginia (USA)**

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## **Introduction**

The sediments and soils in the South River watershed contain elevated concentrations of mercury (Hg) which can be released to the local ecosystem. Studies were conducted at the University of Waterloo to evaluate the effectiveness of passive treatment methods for controlling the release and biological uptake of Hg. The goal of the studies was to evaluate the effectiveness of reactive media to remove or stabilize both dissolved and particulate Hg. The reactive media included in the studies are biochar-based materials, common adsorbents, and other reagents. After initially screening materials for control of inorganic Hg, more detailed studies were conducted to evaluate Hg removal under dynamic flow conditions, potential formation of methyl Hg (MeHg) during treatment, and removal of Hg over longer time frames.

## **Sample Locations**

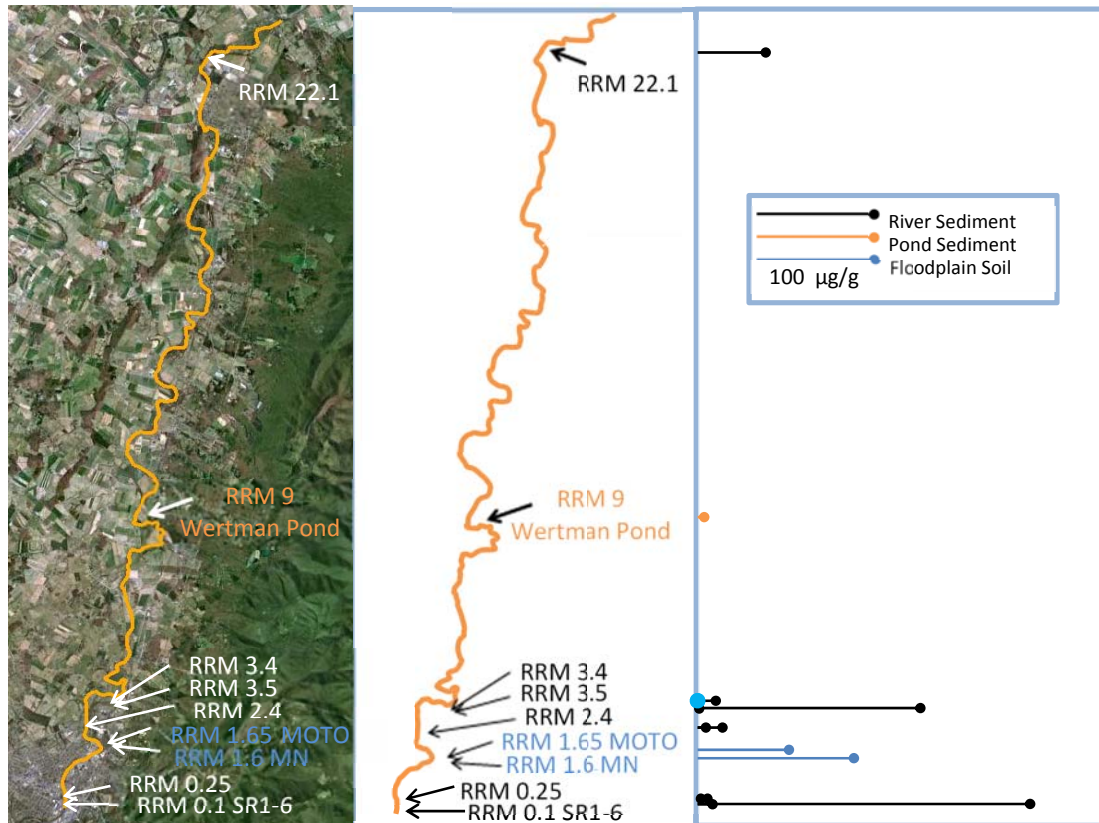
Sediment and soil samples selected for evaluation were collected from the riverbank along the South River and within the floodplain (Figure 1). The treatment experiments focused on sediments and soils with elevated concentrations of Hg from locations RRM 0.1, RRM 1.6, RRM 1.65, RRM 3.5, and RRM 22.1.

## **Overview of Studies**

Analyses were conducted to determine the concentrations and speciation of Hg, bulk chemistry and mineralogy and other chemical parameters for each sediment sample collected. Initial screening studies evaluated the potential for stabilizing Hg using a range of solid-phase reactive media. These studies involved combining reactive media with sediment or soils using batch style experiments, and monitoring the concentration of Hg after a limited mixing time. After the initial screening, more detailed studies were conducted to further evaluate the potential for sustained control of Hg. The studies were designed to answer a series of questions, including:

- a) Do concentrations of Hg decrease in aqueous solutions in contact with sediments that are amended with solid-phase reactive media relative to concentrations in unamended sediments?
- b) Does the addition of reactive media control both dissolved and colloidal forms of Hg?
- c) Does the addition of reactive media control Hg under dynamic flow conditions?
- d) Are the reactions promoted by amendments easily reversed if geochemical conditions change?

- e) Do the concentrations of MeHg decrease in systems containing reactive media?
- f) As the reactive media age, are the reactions reversed, or methylation reactions promoted?



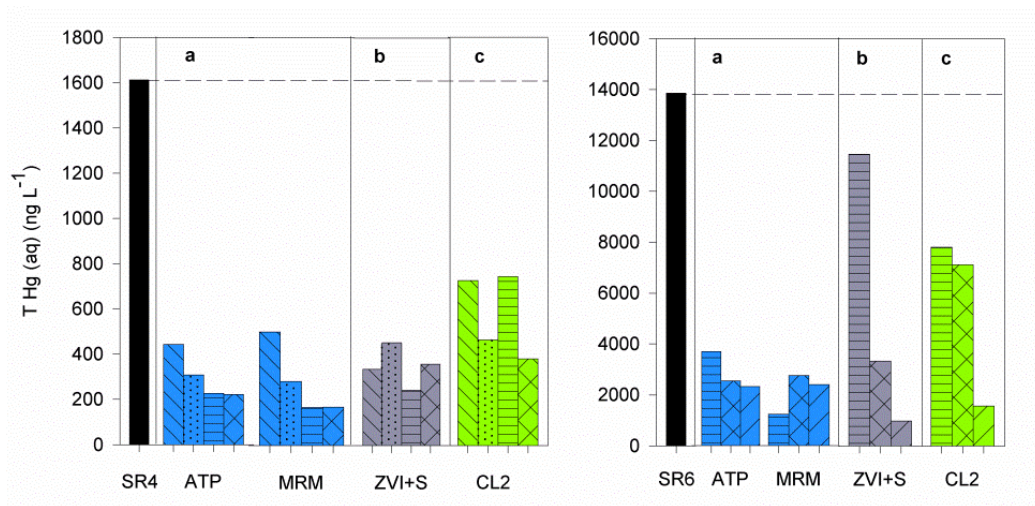
**Figure 1.** Map showing sampling locations, expressed as relative river mile (RRM) downstream from Hg source area, type of sample, and concentrations of total Hg expressed on a dry weight (d.w.) basis.

### **Experiments to Evaluate Hg Control through Addition of Reactive Media Amendments**

Batch experiments were conducted to evaluate the change in Hg release from sediments in response to amendments with solid-phase reactive media. These experiments involved initially mixing South River water and sediment at a 4:1 ratio, followed by the addition of reactive amendments, either as single solids or as combinations of solids. The mixtures were allowed to equilibrate under stagnant conditions for 14 days. After equilibration, the mixtures were gently mixed, and the water sampled for filtered Hg and other geochemical parameters.

For the majority of the mixtures evaluated, the aqueous concentrations of Hg after the addition of reactive media were lower than those observed for the unamended sediment (data not shown). For the amendments which resulted in the greatest reductions in Hg, further testing was completed to evaluate the influence of adding different masses of reactive media to the sediment (Figure 2). For these tests, aqueous concentrations of Hg in contact with the sediments decreased to values that were < 3% to up to 80% of concentrations observed for the unamended sediments (Figure 2). The greatest reductions in Hg concentrations were observed for attapulgite clay,

organically modified clay, and most of the mixtures of zero-valent iron and elemental S. The reductions in Hg concentrations were slightly less for hardwood-based biochar (CL2- Cowboy Charcoal Biochar). The results suggest that, under stagnant conditions, reductions in aqueous Hg concentrations were observed for a range of amendments.

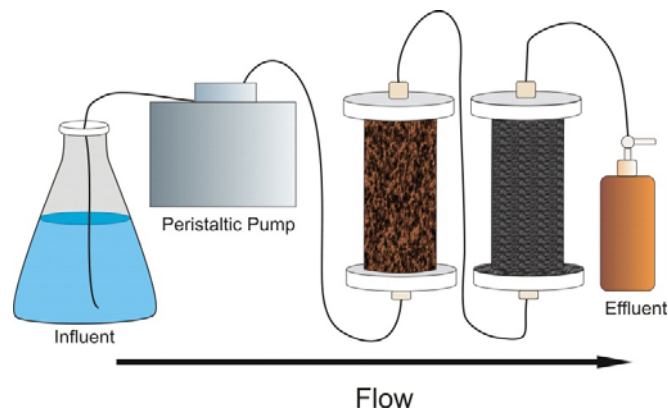


**Figure 2.** Concentrations of Hg after variable masses of reactive material were added to RRM 0.1 samples SR4 (a) and SR6 (b). Black bars indicate the initial Hg concentration without the addition of a reactive-amendment. Diagonal stripes from left-top to right-bottom represent 0.5%, dry weight (d.w.), dots represent 1% d.w., horizontal lines represent 2% d.w., criss-cross represents 5% d.w., and diagonal stripes from right-top to left-bottom represent 8% d.w. ATP=attapulgate clay; MRM = organically modified clay; ZVI = zero-valent iron; S=elemental sulfur; CL2= hard-wood based biochar.

### Experiments to Evaluate Removal of Hg from Flowing Water

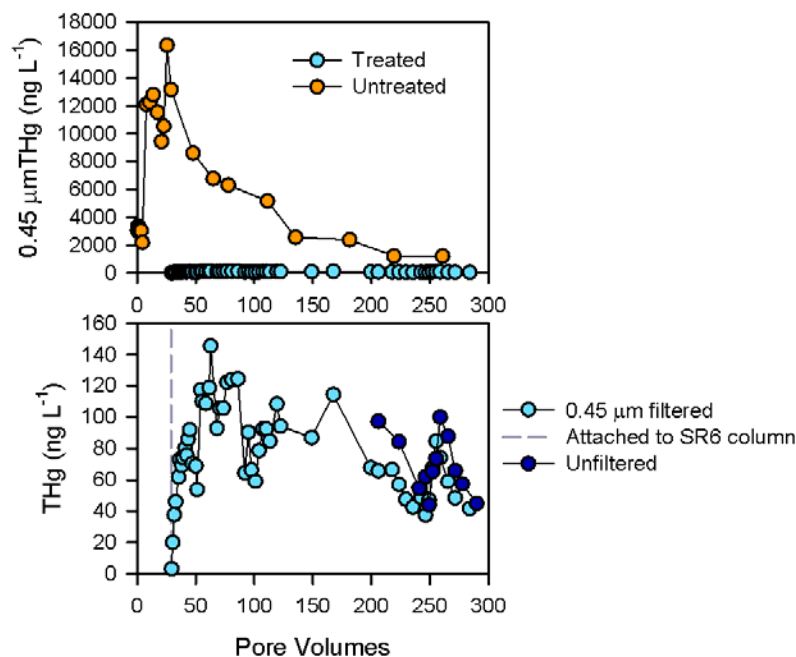
Experiments were conducted to evaluate the potential effectiveness of reactive media at removing discharged Hg under dynamic flow conditions. The experimental apparatus consisted of two columns connected in series; the purpose of column 1 was to simulate Hg leaching from Hg-bearing bank sediment using South River as an input solution and the second column was to remove Hg contained in the effluent of column 1 (Figure 3). Two sets of these combined experiments were conducted. The first columns in these sets contained sediment from RRM 0.1 (SR3 and SR6) and the second columns both contained a mixture of 50% hard-wood based biochar (CL2) and 50% Ottawa sand. This experimental design was selected to provide an indication of treatment effectiveness under continuous Hg loading under flow rates and solid-water ratios typical of field conditions.

The results of the experiments indicate that the total Hg concentrations released from both the SR3 and SR6 leaching columns gradually declined over time. The  $0.45 \mu\text{m}$  filtered Hg declined from 1.8 to  $0.3 \mu\text{g L}^{-1}$  in the SR3 column effluent over 14 months and from 13 to  $2.5 \mu\text{g L}^{-1}$  in the SR6 column effluent over 7 months (Figure 4).



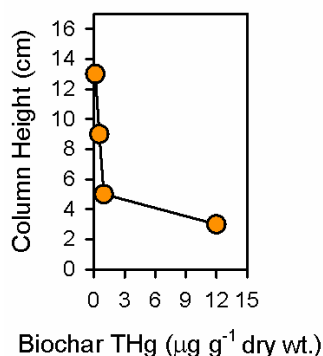
**Figure 3.** Schematic diagram showing experimental design: Effluent from the first column containing sediment is treated using reactive media in a second column connected in series to the first column. The influent was South River water.

The concentrations of Hg in effluent collected from the treatment column attached to the SR3 column were approximately  $20 \text{ ng L}^{-1}$ , representing  $>98\%$  removal of Hg. The concentrations of Hg in effluent collected from the SR6 treatment column reached a maximum of  $146 \text{ ng L}^{-1}$ ; this reduction also represented  $>98\%$  removal of Hg. The treatment effectiveness for these columns



**Figure 4.** Comparison of Hg concentrations in the treated and untreated column effluent for SR6 sediment for  $0.45 \mu\text{m}$  filtered and unfiltered samples over time. Top) Orange symbols show effluent Hg concentrations from the column containing sediment; blue symbols represent effluent from the treatment column. Bottom) Light blue symbols show Hg concentrations for filtered samples and dark blue symbols show the results for unfiltered samples. Note the expanded scale in the bottom diagram.

was sustained over many months of treatment.

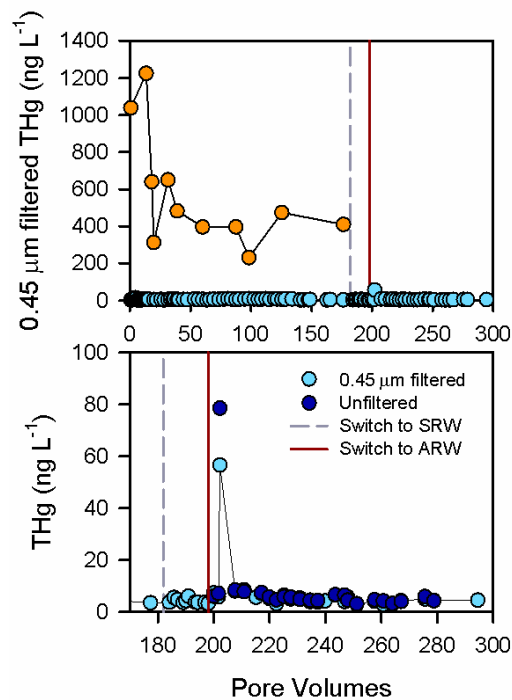


**Figure 5.** Concentrations of THg observed on the biochar solids after sectioning of the SR6 biochar treatment column.

After 314 pore volumes of flow (687 days), the biochar treatment column from the SR6 column was sectioned at 2 cm intervals and the solid biochar analysed for THg and MeHg. The greatest concentration of Hg on the biochar solids was observed on the first 2 cm of material, with a concentration of  $12.0 \mu\text{g g}^{-1}$  (Figure 5). There was a rapid decline in THg concentrations from  $12 \mu\text{g g}^{-1}$  to  $0.97 \mu\text{g g}^{-1}$  by the next 2 cm interval, suggesting the majority of the aqueous Hg was effectively removed within the first 2 cm of biochar material. The first 2 cm of biochar material also was analysed to determine concentrations of MeHg accumulated on the biochar. A solid phase MeHg concentration of  $0.16 \text{ ng g}^{-1}$  was observed on the first 2 cm of material, representing 0.0013% of the THg and not a significant accumulation of MeHg. Additional analyses using synchrotron based techniques currently are underway to identify mechanisms of Hg binding with the biochar material.

After 182 pore volumes of flow, the influent solution from the SR3 sediment was switched to South River water to evaluate the potential for desorption of Hg from the biochar. Very low concentrations of Hg ( $4\text{-}6 \text{ ng L}^{-1}$ ) were observed in the effluent from the treatment column over 16 pore volumes of flow. The input then was switched to simulated acid rain water (denoted by the red vertical line in Figure 6). With the exception of one sample when concentrations of THg approached  $80 \text{ ng L}^{-1}$ , the concentrations remained  $< 10 \text{ ng L}^{-1}$  for an additional 70 pore volumes of flow. These results suggest that the Hg accumulated in the treatment column was strongly bound to the biochar.

The biochar material from the SR3 treatment column was analysed using synchrotron radiation-based XAS techniques at the Argonne National Laboratory, IL, USA. Micro-XRF maps were created from thin sections made from the first 2 cm of biochar material (Figure 7).

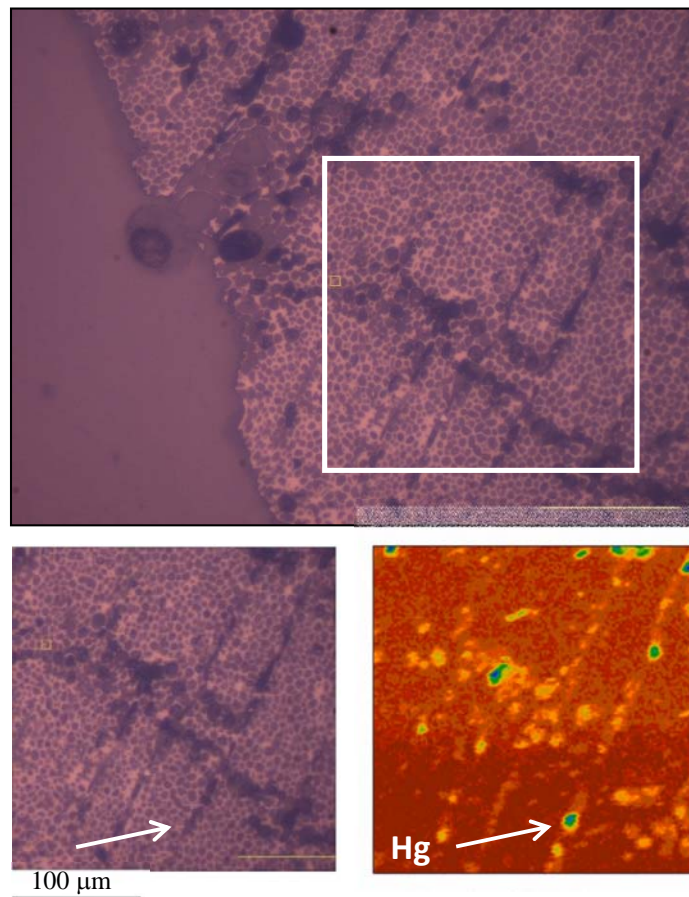


**Figure 6.** Concentrations of Hg in the effluent of treatment column showing nearly complete removal. At ~ 182 pore volumes, the input was switched to South River water (SRW), and then acid rain water (ARW) at 198 pore volumes to evaluate the potential for Hg leaching from the treatment material.

The higher counts of Hg observed in the elemental map appear to correspond to the presence of pore-like areas of the biochar particle. This association suggests these zones in the biochar are more accessible to water containing dissolved Hg, and potentially represent the physical accumulation of Hg-bearing particles. The absence of release of dissolved and particulate Hg from the biochar column observed in the effluent after long-term subjection to ARW suggests that the Hg is strongly bound likely due to a combination of physical and chemical processes.

Experiments are currently in progress to evaluate the effectiveness of co-blending reactive media with sediment from the low-Hg containing riverbank transects under saturated flow conditions.





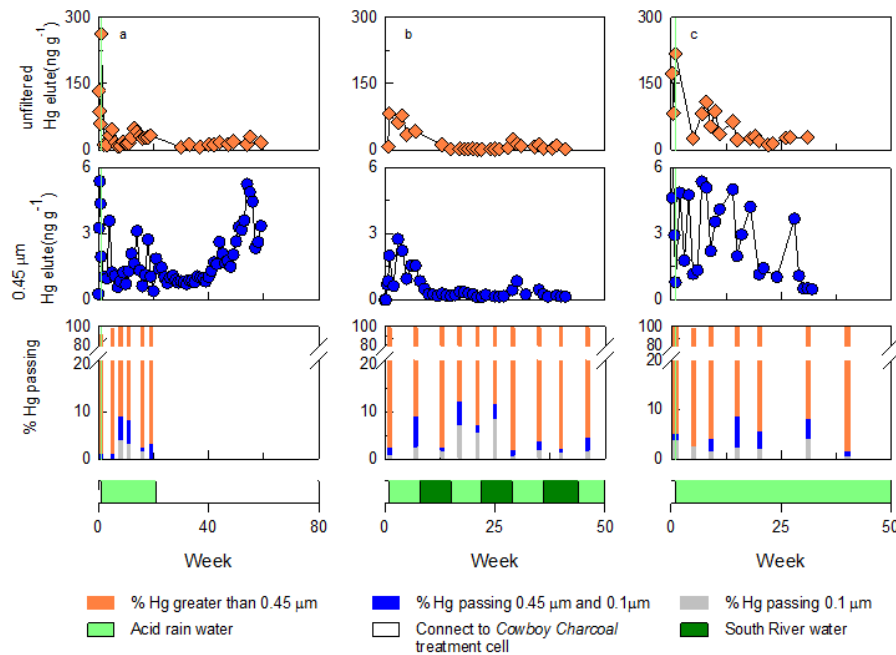
**Figure 7.** Optical image of biochar particle on thin section (top) and zoomed-in (bottom left) with the corresponding  $\mu$ -XRF map of Hg (bottom right) showing hot spots of Hg in green.

### **Experiments to Evaluate Treatment Effectiveness under Variably Saturated Conditions**

Two types of experiments were conducted to evaluate the effectiveness of amending floodplain soil with biochar to limit the release of Hg. These involved experiments in which columns were packed with co-blended mixtures of soil and reactive media, and experiments where effluent from unamended soil was directed through a second column containing reactive media. Each of the cells was subjected to alternating flooding and drying periods following the standard humidity test cell protocol for accelerated weathering (ASTM, 2012).

For the co-blending experiments, humidity cells were packed with a) floodplain soil (RRM 1.65; MOTO) as a control, b) floodplain soil with 16 % dry weight (d.w.) biochar, and c) floodplain soil with 8% d.w. biochar (Figure 8). Either simulated acid rain water or South River water were used to flood the soil mixtures. The results of the experiments indicate that the effluent from the column amended with 8 % biochar had Hg concentrations that were similar to those observed for the unamended soil, suggesting little improvement in Hg control. For the 16 % amendment, the concentrations of Hg were slightly lower than the control, however a direct comparison between the 16% column and the unamended soil was not possible due to differences in flooding

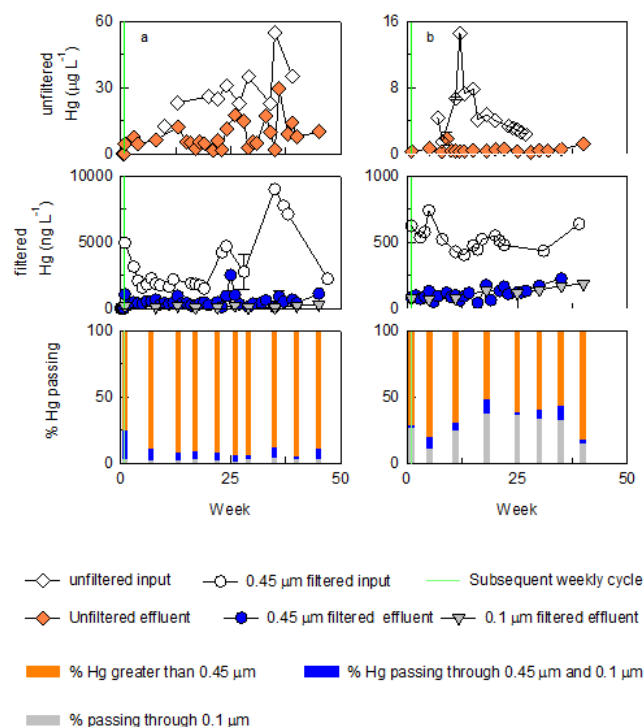
conditions for the two columns. The overall influence of co-blending the soils with biochar appears negligible.



**Figure 8.** Concentrations of Hg, including different filter fractions, in column effluent collected from humidity test cells. a. Floodplain soil, b. Floodplain soil amended with 16 % biochar, and c. Floodplain soil amended with 8% biochar. Note alternating composition of influent solution between simulated acid rain water and South River water.

For the second type of experiments, effluent from cells containing sediment or soil was directed through treatment columns containing a 1:1 mixture of biochar (C12) and Ottawa sand. These columns also were subjected to alternating flooding and drying conditions on a weekly basis. The effluent collected from a cell packed with soil (MOTO) and flooded with simulated acid rain water released elevated concentrations of Hg, up to  $60 \mu\text{g L}^{-1}$  unfiltered Hg, and up to  $10 \mu\text{g L}^{-1}$  filtered Hg (Figure 10a). After directing this effluent through a treatment column, 70% of the particulate Hg and 68% of  $0.45 \mu\text{m}$  filtered Hg was removed by the biochar treatment column. For riverbank sediment (SR6) flooded with South River water, concentrations of Hg also were highly variable with effluent concentrations reaching maximum values of  $15 \mu\text{g L}^{-1}$  unfiltered Hg and  $750 \text{ng L}^{-1}$  filtered Hg. After directing this effluent through the treatment column, approximately 90% of the particulate Hg and 80% of the  $0.45 \mu\text{m}$  filtered Hg was removed (Figure 9b). These results suggest that biochar may be an effective material for removing Hg under rapid flow conditions.





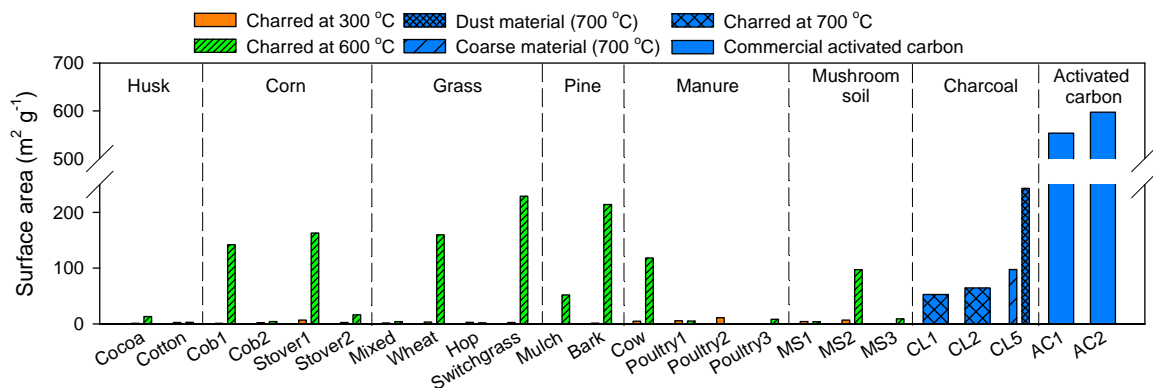
**Figure 9.** Concentrations of Hg in the effluent from a) floodplain soil (MOTO) flushed with acid rain water and b) riverbank sediment (RRM 0.1 SR6) flushed with South River water (open symbols), and concentrations of Hg in the effluent from the treatment cells for a) effluent from MOTO cell and b) effluent from SR6 cell (coloured symbols).

### Experiments to Evaluate a Broad Range of Biochar Materials for Hg Control

Laboratory experiments were conducted to evaluate the effectiveness of a broader range of biochar materials for removing Hg from water. Thirty-nine biochar materials were prepared from different source materials and pyrolyzed at two temperatures. The biochars were characterized for properties which might influence the extent of Hg uptake and potential use in field settings. These properties include bulk density, particle-size distribution, specific surface area, carbon and sulfur content, surface functional groups, surface morphology and chemical composition. Measurements of Hg uptake were made using batch-style equilibration experiments. The biochar samples were added at a 1:75 mass ratio to South River water spiked with  $10 \mu\text{g L}^{-1}$  Hg added as a  $\text{HgCl}_2$  salt. The spiked river water and biochar were mixed thoroughly, and then allowed to settle and equilibrate. After equilibration, water samples were passed through  $0.45 \mu\text{m}$  filters and analysed for pH, alkalinity and aqueous concentrations of Hg, dissolved metals, anions, nutrients, short-chain organic acids and dissolved organic matter.

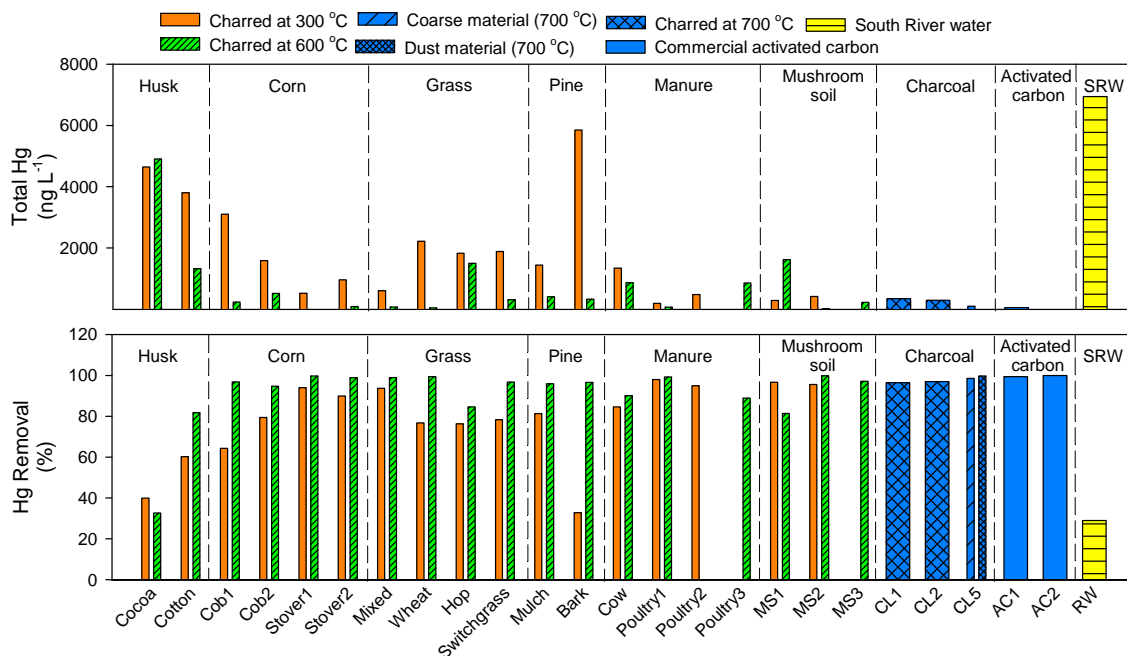
The specific surface area (SSA) varied substantially for the different biochars. The SSAs for biochars prepared at  $300 \text{ }^\circ\text{C}$  varied from  $1.06$  to  $11.3 \text{ m}^2 \text{ g}^{-1}$ , much lower than those for charcoal and granular activated carbon, which had SSAs ranging from  $1.93$  to  $597 \text{ m}^2 \text{ g}^{-1}$  (Figure 10). The SSAs of biochars pyrolyzed at  $600 \text{ }^\circ\text{C}$  also varied substantially from  $1.93$  to  $229 \text{ m}^2 \text{ g}^{-1}$ . The

feedstocks did not appear to play a key role in the SSA values, but the preparation temperatures did. The ratio of SSA of biochars prepared at 600 °C over that of biochars prepared at 300 °C ranged between 0.67 and 131.



**Figure 10.** Specific surface areas (SSA) of biochar samples.

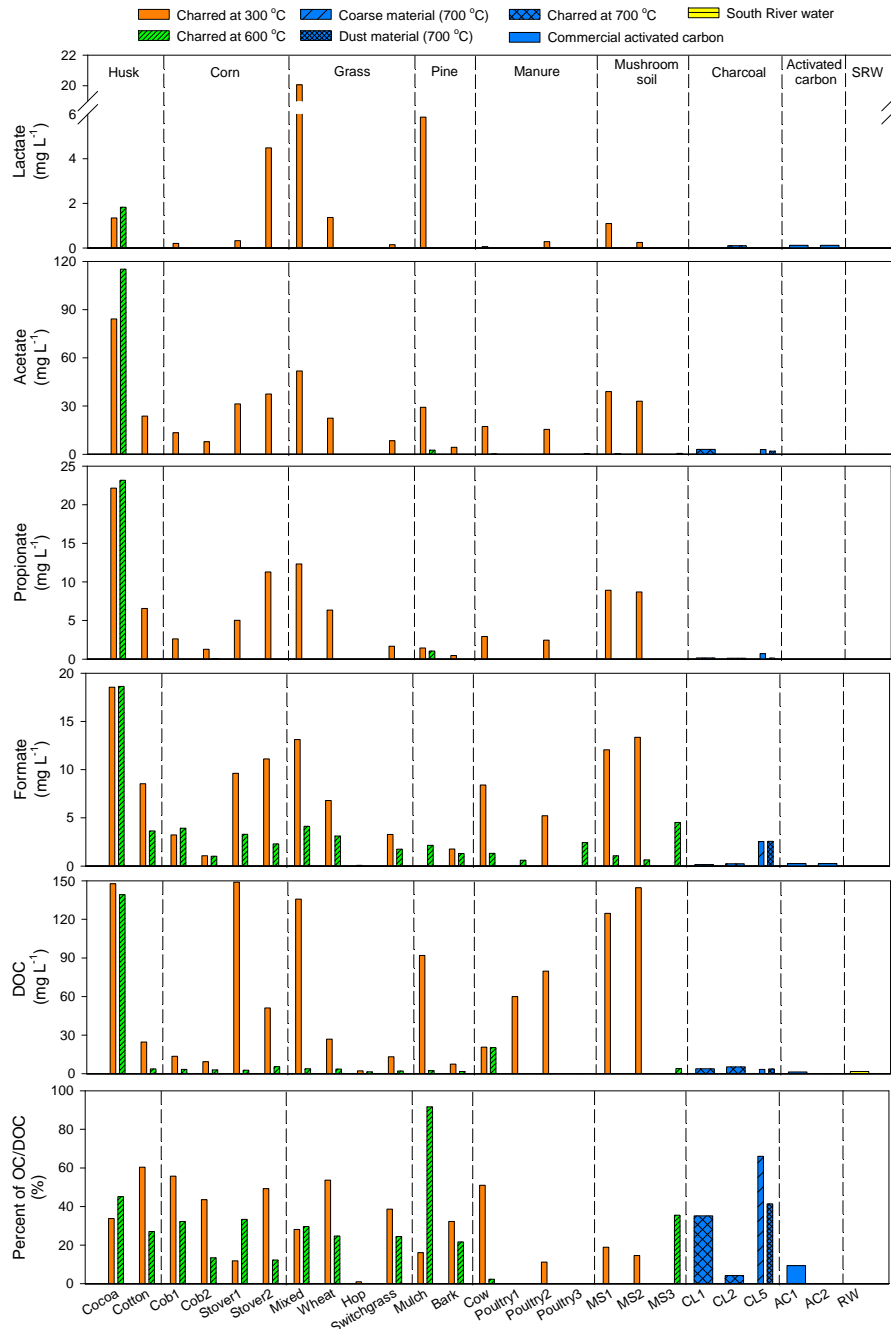
In the aqueous treatment systems, concentrations of Hg decreased by > 90% in the mixtures containing activated carbon, charcoal and biochars pyrolyzed at 600 °C (Figure 11). In the systems containing other biochars, concentrations of Hg decreased by 40-90%, with the lowest removals observed for biochars made from husk, corn and pine bark prepared at low temperature. In this study, the higher removal rates corresponded to higher surface area material, which is consistent with literature studies which often show a positive correlation between surface area and treatment efficiency.



**Figure 11.** Concentrations of total Hg and % removal for mixtures containing biochar and Hg spiked South River water.

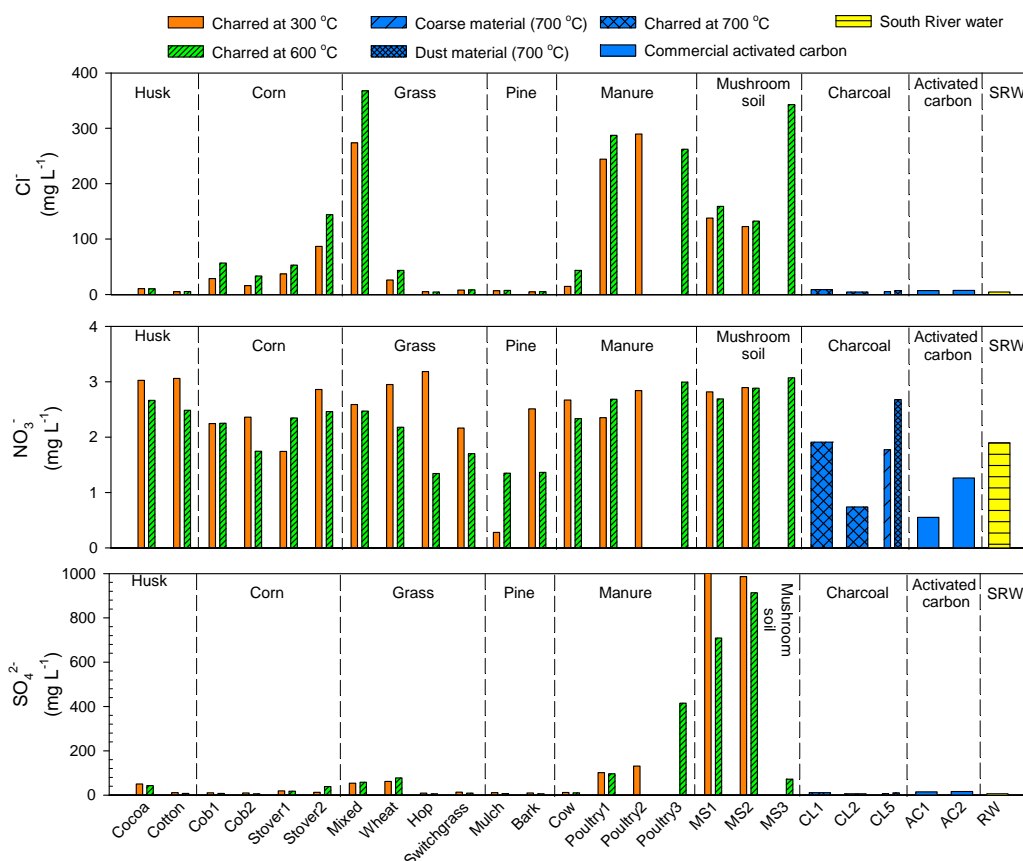
A number of substances can be released from biochars which can contribute to soil fertility (e.g. nutrients) (Lehman and Joseph, 2009), but also can stimulate microorganisms which methylate

Hg (e.g. Gilmour et al., 1992). The activities of Hg methylators are greatest in reducing systems which contain elevated concentrations of labile electron donors (e.g. short chain organic acids) and  $\text{SO}_4^{2-}$  as an electron acceptor. In this study, the release of short-chain organic acids, nutrients and sulfate was monitored for the different biochar samples. The release of short-chained organic acids was observed to vary with feedstock and pyrolysis temperature (Figure 12), with the greatest concentrations observed for the biochars prepared at 300 °C and for husk, corn, grass, and mushroom soil.



**Figure 12.** Concentrations of organic acids and total dissolved organic carbon for aqueous solutions mixed with biochars.

Concentrations of  $\text{Cl}^-$  were variable for the different groups of biochars, with slightly higher concentrations observed for the higher temperature biochars. In contrast, the concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were higher for the lower temperature biochars (Figure 13). The release of  $\text{Cl}^-$  was greatest for corn, grass, manure and mushroom-soil biochars. The release of  $\text{NO}_3^-$  was more consistent across the groups. Concentrations of  $\text{SO}_4^{2-}$  were highly variable, with elevated concentrations observed for grass, manure and especially mushroom-soil based biochars.



**Figure 13.** Aqueous concentrations of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  for river water mixed with biochars.

The results of these studies on different types of biochars indicate variable Hg uptake, and highly variable release of short-chained organic acids and sulfate. Some biochars evaluated in this study, such as biochar produced from hardwood, showed high Hg uptake with limited release of substances which can stimulate methylation reactions. In contrast, some biochars, such as biochar produced from mushroom soil, released elevated concentrations of  $\text{SO}_4^{2-}$ , which could promote methylation reactions in the presence of labile organic carbon sources. Others promoted the release of nutrients which could be used to enhance growth of plants in agricultural settings.

## **Summary**

Studies were conducted to evaluate the potential removal of Hg from water and stabilization of Hg in sediment and soils under static and dynamic flow conditions. More detailed studies were focused on solid-phase reactive media which are readily available and provide sustained removal

or stabilization of Hg. The studies also included assessment of Hg methylation potential through the direct measurement of MeHg or through analysis of substances which can stimulate methylation reactions. Some of the main findings of the studies suggest that a number of solid-phase reactive media can remove aqueous phase Hg. However, although some reactive media have the potential to remove Hg, they also appear to have the potential to stimulate methylation reactions. Further studies are focused on evaluating the long-term effectiveness of reactive media at limiting Hg concentrations and at suppressing the generation of MeHg. Alternative treatment approaches also are being evaluated.

## **References**

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Lehmann, J., Joseph, S., 2009. *Biochar for Environmental Management: Science and Technology*. Earthscan Publishers, London, UK