

Evaluation of inorganic and carbon-based materials for mercury stabilization when co-blended with contaminated river sediment: A column study

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INTRODUCTION

In riverine environments, mercury (Hg) contamination derived from mining or industrial processes can persist long after direct Hg inputs have ceased. In many instances, complete removal of Hg-contaminated soils and sediments from affected riverbanks and floodplains is not feasible due to the widespread occurrence of Hg downstream of the initial source; instead, *in situ* remediation techniques can be employed to immobilize Hg and render it less bioavailable. The application of sorptive and/or reactive amendments to contaminated soil or sediment is an example of an *in situ* remediation technique that can be applied on a large scale [1,2]. These amendment materials can be blended into soil or sediment and serve to sequester Hg, minimizing the effects of physical and chemical perturbations on Hg release (Fig. 1).

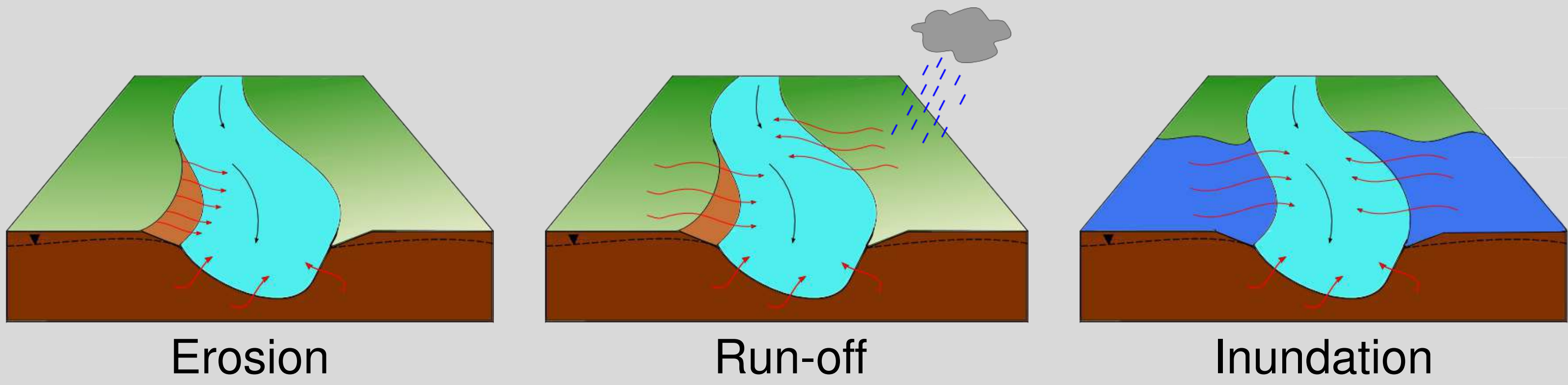


Figure 1. Physical perturbations that can influence Hg release from contaminated soil and sediment include riverbank erosion, surface run-off, inundation by floodwaters and groundwater seepage.

In this study, saturated column experiments were conducted to evaluate the effects of several carbon-based (biochar) and inorganic (limestone, attapulgite clay) amendments on Hg transport and bioavailability. Both biochar and attapulgite clay were selected due to the high sorption potential associated with each material, while limestone was chosen as a result of its ubiquity in the agricultural industry as a soil amendment. Modification of the biochar and attapulgite clay amendments was employed to alter the physiochemical properties of the materials, rendering them more effective for Hg sequestration.

RESEARCH QUESTION

Can effective treatment of Hg-contaminated sediment be achieved through blending with different reactive media?

- What are the effects of inorganic amendments on Hg transport and MeHg production in contaminated sediment?
- Can biochar – both modified and unmodified – be an effective material for Hg remediation when co-blended with sediment?

RESULTS AND DISCUSSION

Cumulative Hg Release – Inorganic Amendments

- Addition of limestone to contaminated sediment had little effect on Hg mobilization relative to the Control
- Enhanced transport of Hg was observed when sediment was blended with unmodified clay (Fig. 3)
 - Cumulative filter-passing (<0.45 µm) Hg measured in the Clay column effluent increased by more than 200% when compared to the Control
- Reduced transport of Hg was observed when sediment was blended with sulfidized clay
 - Cumulative filter-passing Hg measured in the effluent of the S-Clay column was 24% of the Control

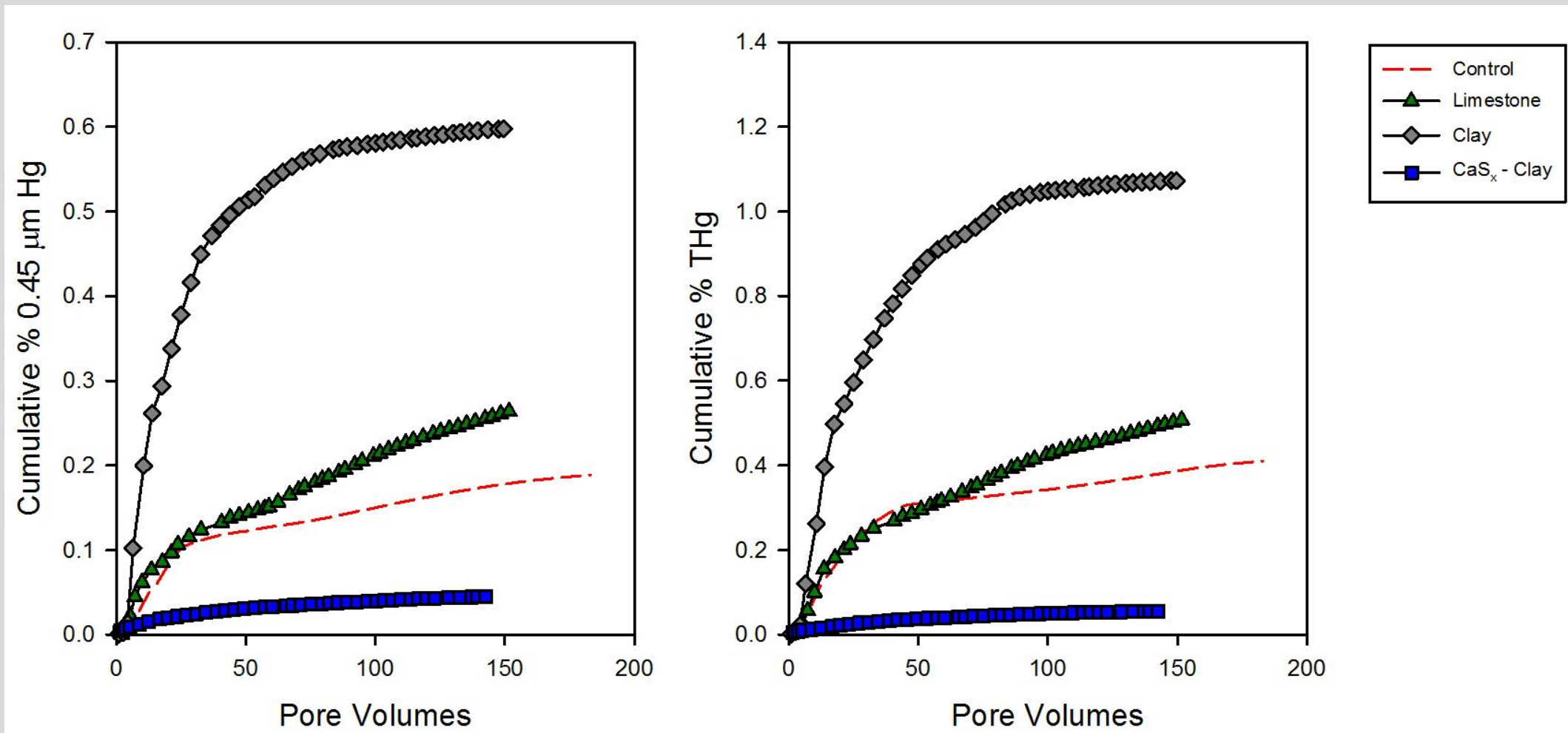


Figure 3. Cumulative 0.45 µm filtered Hg (left) and cumulative unfiltered total Hg (right) measured in the effluent of the inorganic amendment columns.

Cumulative Hg Release – Biochars

- Minimal influence on Hg transport was observed when contaminated sediment was blended with unmodified or HNO₃-modified biochar (Fig. 4)
- Cumulative leaching of filter-passing Hg was greatly reduced in both columns containing sediment blended with sulfidized biochar
 - When a 2% dosage of sulfidized biochar was applied, cumulative effluent Hg concentrations decreased by 71% relative to the Control
 - Increasing the dosage of sulfidized biochar to 5% resulted in greater Hg sequestration, yielding an 83% reduction in Hg leaching

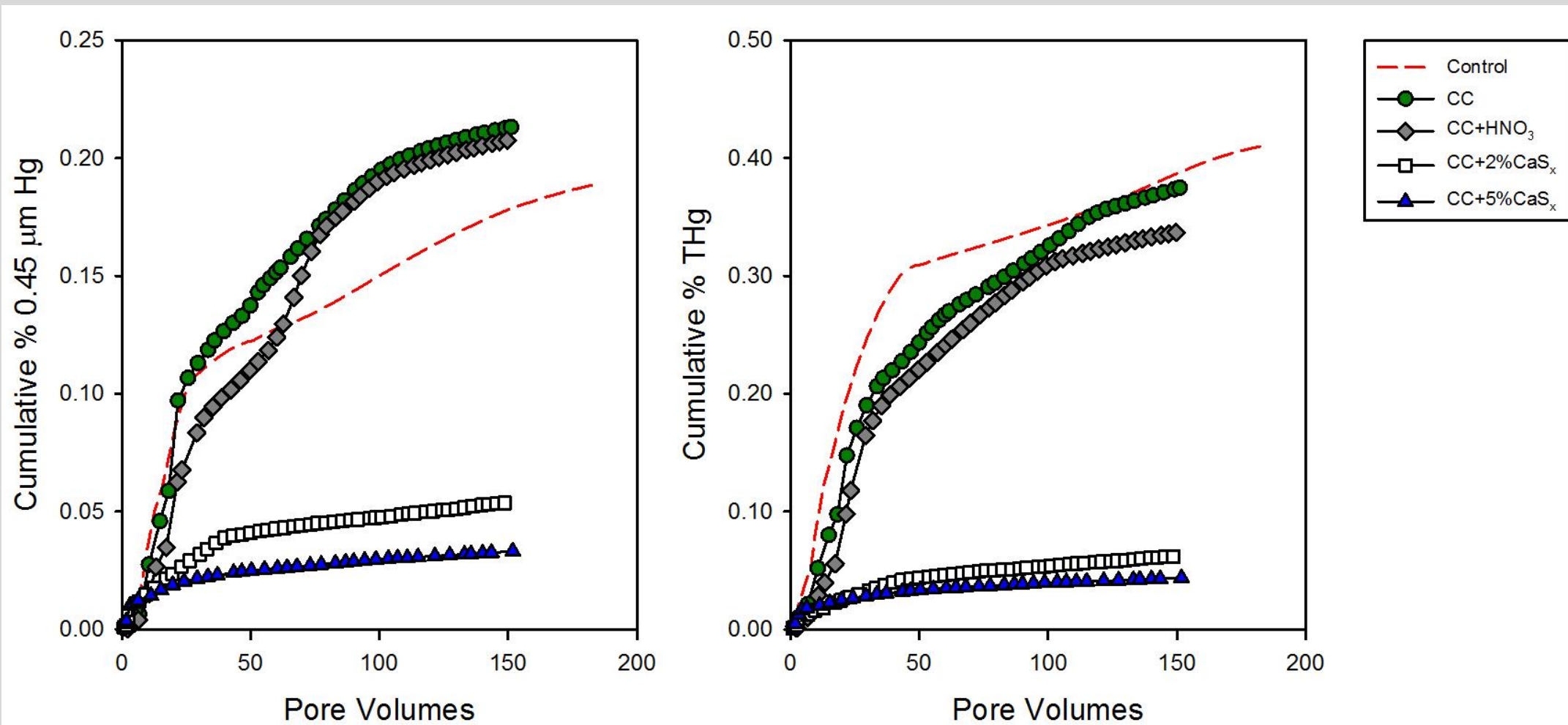


Figure 4. Cumulative 0.45 µm filtered Hg (left) and cumulative unfiltered total Hg (right) measured in the effluent of the biochar columns.

Methylmercury

- Net MeHg production was not appreciably altered by the addition of most amendment materials (Fig. 5)
- Elevated concentrations of MeHg were observed in the effluent of the Clay column
 - Peak aqueous MeHg was 30 ng L⁻¹ in the Clay column effluent as compared to 7 ng L⁻¹ measured in the Control column effluent
 - The increase in aqueous MeHg observed with the clay amendment may have resulted from colloid-facilitated transport or destabilization and methylation of previously sediment-bound Hg

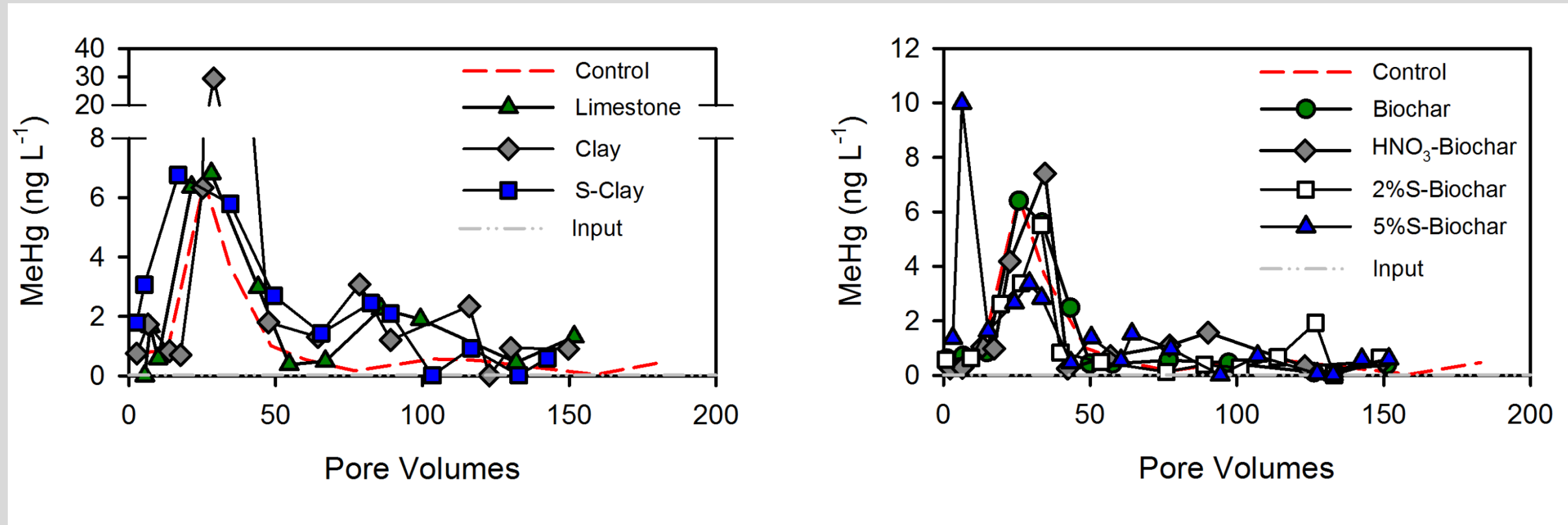


Figure 5. Aqueous MeHg concentrations measured in the effluent of the inorganic amendment columns (left) and biochar columns (right).

CONCLUSIONS

- Minimal impact on Hg transport was observed with the addition of limestone, biochar and HNO₃-modified biochar to contaminated sediment
- Hg mobilization and MeHg production were increased in the presence of unmodified clay
- Sulfidation of clay and biochar enhanced the Hg uptake capacity of both materials
- Blending reactive materials with contaminated sediment can stabilize Hg under saturated conditions

EXPERIMENTAL METHODS

Amendment Modification

- Biochar soaked in nitric acid to increase metal-chelating functional groups
- Biochar and attapulgite clay soaked in a sulfur solution to impart sulfur-containing functional groups

Saturated Column Experiments

- Mercury-contaminated sediment was collected from a riverbank along the South River, VA
 - Historical release of Hg from a textile plant in Waynesboro, VA, USA resulted in widespread contamination of riverbank sediments and floodplain soils within the South River watershed
- Sediment was blended with a 2% or 5% (dry weight) dosage of a given amendment material and wet-packed into acrylic columns (15 cm x 4 cm) (Fig. 2)
- Water taken from the South River, upstream of the Hg-release site, was pumped upwards through the columns for approximately 150 pore volumes (PV) (Table 1)
- Aqueous samples were collected from the column effluent and analyzed regularly for Hg and methyl mercury (MeHg) using standard EPA methods, as well as other parameters.

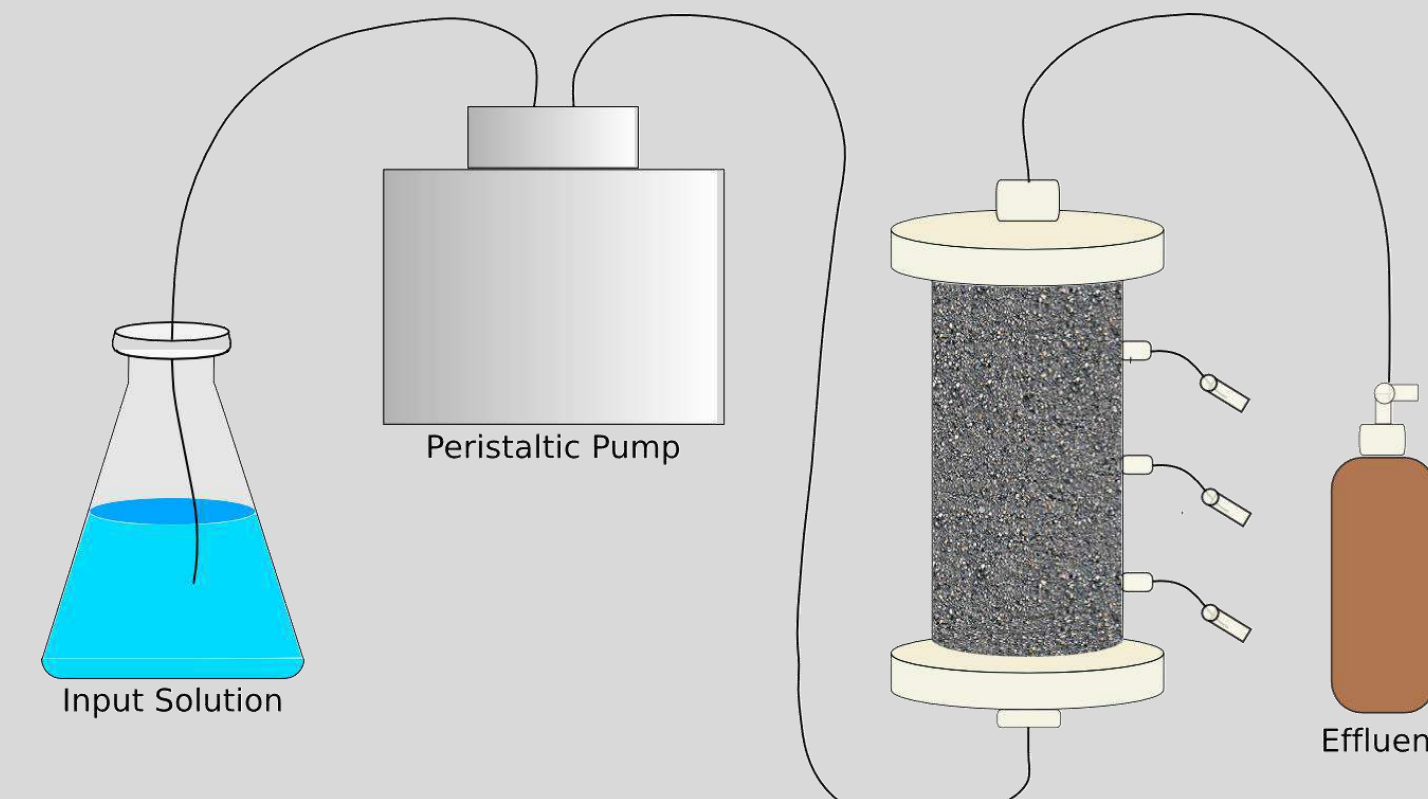


Figure 2. Schematic diagram of a saturated column experiment

Table 1. Summary of amendments and flow parameters for column experiments

		Inorganic Amendments			Biochars			
Column ID	Control	Limestone	Clay	S-Clay	Biochar	HNO ₃ -Biochar	2%S-Biochar	5%S-Biochar
Material	N/A	Agricultural limestone	Attapulgite clay	S-modified clay	Biochar	HNO ₃ -modified biochar	S-modified biochar	
Dosage (dry weight)	N/A	2%						5%
Final PV	187	154	153	145	155	154	152	155
Duration (Weeks)	47	46	44	41	45	44	47	36

REFERENCES AND ACKNOWLEDGEMENTS

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Acknowledgements

This research was funded by DuPont, an NSERC Collaborative Research and Development Program grant, and an Ontario Research Fund – Research Excellence grant. Thank you to Erin Mack, Nancy Grosso and Jim Dyer of DuPont, the South River Science Team and to Jing Ma for their contributions to this research.