

STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Evaluation of Sorbent Effectiveness in the Presence of Particulate Mercury Species

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EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Development Initiative, an innovative program developed by the U.S. Department of Energy's Office of Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2022, a DOE Fellow intern, Caridad Estrada Cardona, spent 10 weeks doing a summer internship at the Oak Ridge National Laboratory under the supervision and guidance of Dr. Alexander Johs, R&D Staff Scientist in the Environmental Sciences Division. The intern's project was initiated on June 6, 2022, and continued through August 12, 2022 with the objective of evaluate geochemical factors that control the performance of engineered sorbent materials for the sorption of mercury in freshwater stream banks and sediments. Laboratory experiments were conducted to evaluate the role of Hg speciation on sorbent efficiency in a series column experiments in the Aquatic Ecology Laboratory (AEL) at ORNL.

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1. INTRODUCTION

Mercury (Hg) is an environmental pollutant that behaves differently in the environment depending on the chemical species present. Therefore, chemical speciation of mercury has emerged as an important factor controlling mercury behavior and risk in environmental and industrial systems. East Fork Poplar Creek (EFPC) in Oak Ridge, TN, receives inputs of mercury caused by legacy contamination at the Department of Energy (DOE) Y-12 National Security Complex (Brooks and Southworth 2011). Mercury (Hg) behaves differently in the environment depending on the chemical species present. Remediation of Hg-contaminated ecosystems constitutes a significant long-term challenge, because even low-level Hg contamination can result in production of methylmercury (MeHg), which is a potent neurotoxin (Clarkson 1998, Korbas, O'Donoghue et al. 2010). Methylmercury biomagnifies and bioaccumulates up trophic levels in aquatic food webs affecting many ecological receptors (Chen, Serrell et al. 2008). Human exposure to MeHg is a public health concern and is predominantly caused by the consumption of contaminated fish (Mergler, Anderson et al. 2007).

The industrial use of Hg at the Y-12 National Security Complex in Oak Ridge, TN resulted in losses of elemental Hg to the environment. Approximately 128,000 kg of Hg entered East Fork Poplar Creek (EFPC) over the period from 1950 to 1963 (Southworth, Greeley Jr et al. 2010, Brooks and Southworth 2011). After the industrial use of Hg ended, annual mercury releases from Y-12 decreased substantially. However, lower-level mercury discharges continued from the facility because of past spills near buildings that contaminated surrounding soils and storm drains. Despite significant past remediation efforts to remove Hg from floodplain soils, large quantities of Hg-contaminated soils and sediments remain in the downstream environment. Legacy Hg contamination in creek banks, floodplain soils, and stream sediments downstream of Y-12 accounts for the majority of the annual export of mercury to the EFPC watershed. Past studies suggest that approximately 85% of the mercury inventory is associated with floodplain and creekbank soils on the 18 km reach of Lower East Fork Poplar Creek (LEFPC), which extends from the boundary of Y-12 downstream to the mouth of the EFPC (Southworth, Greeley Jr et al. 2010, Southworth, Mathews et al. 2013). Hg concentrations in LEFPC floodplain soils are generally higher in the upper third of the creek and show high variability depending on location. Longitudinal surveys yielded a better understanding of the distribution, speciation, and mobility of Hg contamination in LEFPC. Floodplain soils contain Hg, primarily in the form of mercury sulfides (HgS), in concentrations up to 400 mg Hg/kg soil (Dickson, Mayes et al. 2019). Along the creekbanks even higher Hg concentrations are present within a 5 to 46 cm thick layer, which is referred to as the historical release deposit (HRD). The HRD layer contains fly ash, coal fines and a legacy of discrete mercury-rich particles embedded in fine-grained soils with Hg concentrations reaching up to 4,600 mg/kg (Goñez-Rodríguez, Johs et al. 2021). Erosion of bank soils and specifically the HRD soil layer represents an essential input of Hg into EFPC (Watson, Brooks et al. 2016). The flux of total Hg from bank erosion in LEFPC was estimated to reach 38.6 kg/yr based on measurements of streambank erosion, while the total annual flux estimate for Hg in the creek is 98 kg/yr at a distance of 5.4 km upstream from the mouth of LEFPC (Riscassi, Miller et al. 2016).

Mercury deposits in LEFPC bank soils including the HRD are a persistent source for in-stream production of MeHg by aquatic microorganisms. These deposits are present in several chemical

forms, e.g. Hg(II) complexed with natural organic matter (Hg-NOM), as mercury sulfide (HgS) particles and elemental mercury (Hg⁰). Therefore, chemical speciation of mercury has emerged as an important factor controlling mercury behavior and risk. These Hg species are subject to varying degrees of mobilization, redox transformations, and release into the stream channel due to dynamic environmental conditions, such bank erosion as a result of rain events and flooding, seasonal temperature changes, changes in vegetation or microbial activity (Koenigsmark, Chiu et al. 2023). Thus, Hg remediation efforts are focused on source control to limit mobilization of Hg from banks and sediments with the intent of limit MeHg production and transfer into food webs.

Sorbent amendments are considered a low-impact alternative to dredging and capping for the remediation of soil and sediments on Hg-contaminated sites (Gilmour, Riedel et al. 2013). Nevertheless, the number of field studies applying sorbents for Hg remediation is limited. Engineered sorbents are widely used for the removal of heavy metals from industrial waste streams and for in situ stabilization. Previous sorbent studies demonstrated that Hg sorption is affected by Hg speciation, particularly dissolved organic matter (DOM), which is abundant in LEFPC (Johs, Eller et al. 2019). The effectiveness of remediation strategies employing sorbent technologies for mitigating the release of Hg from contaminated bank soils is governed by the partitioning of the contaminant between contaminated soils or sediments and potential sorbent materials. A significant fraction of Hg inventories in LEFPC floodplain soils is present as metacinnabar (β -HgS). Erosion can release particulates with significant mass fractions of HgS into the creek. The reported equilibrium constant ($\log K$) for the dissolution of β -HgS ($\text{HgS}_{(s)} + \text{H}^+ \rightleftharpoons \text{Hg}^{2+} + \text{HS}^-$) is -36.8 ± 0.1 at a temperature of 25 °C, pH 7.0 and ionic strength $I = 0$ (Drott, Bjorn et al. 2013). Because of the low solubility of these minerals, HgS-rich particulates are expected to persist in EFPC. Previous column experiments with soil leachates from LEFPC bank soils indicated the presence of Hg species that weakly interact with the sorbent material suggesting a potential role for particulate HgS (Goñez-Rodríguez, Johs et al. 2021). Therefore, evaluating the effectiveness of sorbents on the removal of HgS particulates is essential for identifying successful remediation strategies for contaminated bank soils.

Project scope

The overall goal of the project is to investigate the distribution and mobility of Hg species in LEFPC and how they interact with engineered sorbents. This study aims to evaluate the role of Hg speciation and other geochemical factors that control the performance of engineered sorbent materials for the sorption of mercury in freshwater stream banks and sediments in a series of column experiments in the Aquatic Ecology Laboratory (AEL) at ORNL. Experimental data were collected to obtain parameters for predictive modeling using the following methods:

The advection-dispersion equation (ADE) is a partial differential equation that can be used to model contaminant transport in porous media. It describes the directional movement of the fluid carrying the contaminant and the spread of solutes through random motion and mixing (Parker and Van Genuchten 1984). Here, we use the ADE to describe the movement of Hg species as they travel through sorbent-packed micro columns while the mobile phase represents the water chemistry of the actual creek.

Pore volume – Dispersion caused by variations in pore water velocity is imperative to calculate and model pore volumes of various sorbents as they are made from different materials. These pore volumes aid us with our predictive ADE model implemented in Python.

In order to measure solute flow and to determine transport parameters of the sorbent columns, we used bromide as a conservative tracer. Zinc sulfide (particle transport) and various filters. We are also exploring the mechanism by which sorbents collect particles. In theory it is mainly filtration (quartz sand is proof of this).

The goal of this study was to evaluate several sorbent materials for the removal of Hg from aqueous media. Mercury can exist in different chemical species, which have different properties and behaviors in the environment. A large fraction of Hg in LEFPC is associated with particles, such as mercury sulfides or organic matter-bound Hg, which enter the stream from creek and sediments. A combination of techniques analyzed in this study could be economically feasible and practical to reduce the concentration of mercury in LEFPC. The results from these studies considering the effect of Hg speciation on engineered sorbents will inform remediation strategies for LEFPC.

Hypotheses:

- The removal of particulate Hg species by engineered sorbents is predominantly driven by a depth filter effect, which traps particles along the flow path through the sorbent material.
- Particle size controls retention of particulate Hg species in sorbent columns. Smaller (colloidal) particles are more likely to pass through the column compared to larger particles.
- A substantial fraction of particulate Hg species present in LEFPC creek water can be removed by passing the water through simple filter media (e.g. clean quartz sand)
- Long-term use of sorbents in the presence of creek water may result in the partial conversion of HgS and other Hg(II) species into other dissolved Hg species as a result of microbial redox processes.

2. RESEARCH DESCRIPTION

Materials and Methods

Sorbents

Biochar is produced by slow pyrolysis of Colorado pine softwood at 650 °C (BiocharNow, LLC, Loveland, CO, USA). Organoclay PM-199 (CETCO, Hoffman Estates, IL, USA) is a phyllosilicate clay modified with organocations and is commonly used for the remediation of hydrophobic organics. Filtrasorb 300 is a granular activated carbon made from bituminous coal with high abrasion resistance and is commonly used in municipal and industrial water treatment applications (Calgon Carbon Corporation, Pittsburg, Pennsylvania, USA).

Micro-Column Experiments

Sorbent columns were used to evaluate solute transport and Hg breakthrough. Two sorbent and one quartz sand (IOTA, Unimin Corp., New Canaan, CT, USA) columns were constructed. The sorbents were packed into polycarbonate flow columns, having an inner diameter of 2 cm and a length of 9.2 cm. A small amount of glass wool was applied at the bottom, the sorbent and sand columns were packed by slowly adding each sorbent or sand while tapping the columns to minimize the formation of void spaces. Finally, a layer of glass wool was inserted at the column effluent. After assembly, the sorbent columns were purged with CO₂ for about 1 minute from the bottom to displace the air inside the column and prevent the formation of gas bubbles that can cause preferential flow (Xue, Chen et al. 1997). An artificial creek water (ACW) solution representing the water chemistry of LEFPC (Table 1) was used for all experiments. A schematic representation of the experimental setup is shown in Figure 1. Sorbent column influent solutions were connected to a Masterflex® L/S® (Cole-Parmer, Antylia Scientific Co., Vernon Hills, IL, USA) standard digital pump with a multichannel cartridge pump head to introduce the ACW to the bottom of the column at a flow rate of 60 mL·h⁻¹ in order to fill and saturate the column. The complete sorbent column setup including inlet solution reservoir, tubing, peristaltic pump, valves, and column is shown in Figure 2.

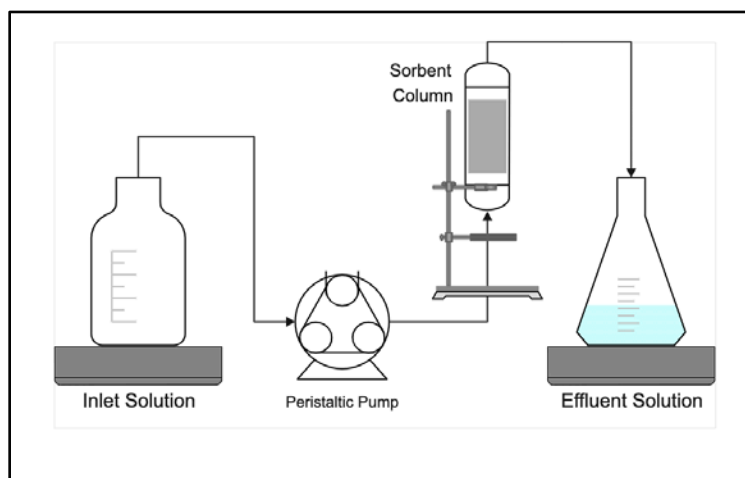


Figure 1 - Model diagram of sorbent column setup (not to scale)

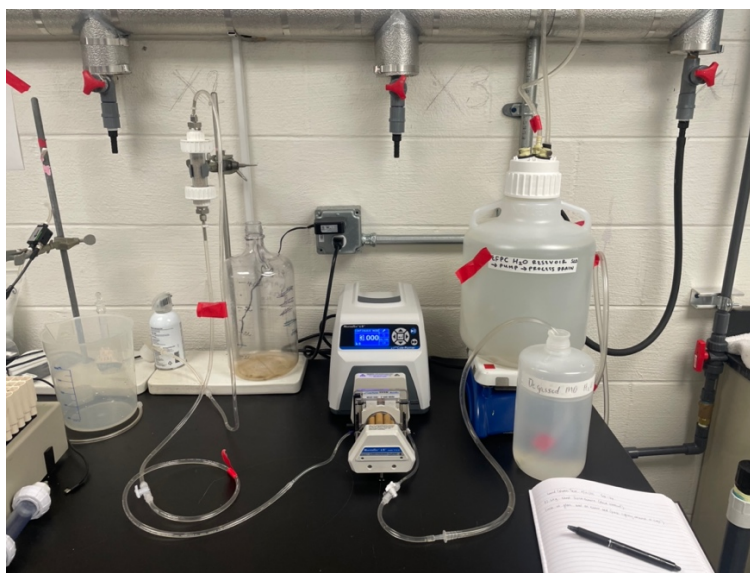


Figure 2 – Sorbent column setup

Table 1 - Chemical composition of artificial creek water (ACW), final pH 7.8

Component	Conc. [mM]
Ca ²⁺	1.035
Mg ²⁺	0.496
Na ⁺	1.191
K ⁺	0.048
Cl ⁻	0.418
SO ₄ ²⁻	0.353
NO ₃ ²⁻	3.178

Nonreactive Tracer Experiments

Nonreactive tracer experiments were conducted in the sorbent and sand columns using bromide (Br⁻) to create a predictive transport model of each column. The Br⁻ data are presented in relative pore volumes, which represents the volume of solution eluted compared to the total pore volume of the saturated pores in the columns; thus, one pore volume means that the amount of solution displaced is equivalent to the volume of water inside the sorbent column (Table 2). A three-way valve at the lower sorbent column boundary was used to make an instantaneous switch from the flowing ACW to a flowing solution of ACW with 10 mg·L⁻¹ Br⁻ added as KBr, using two different pumps each set to a flow of 1 mL·min⁻¹. Bromide was passed through each sand and sorbent column until Br⁻ was detected, and effluent samples of 4 mL each were collected using a Spectra/Chrom CF-2 fraction collector (Spectrum Chromatography, Houston, TX, USA). After 2 h, the valve was switched back to the ACW to allow all the applied Br⁻ to elute, while still collecting samples with the fraction collector. After the Br⁻ experiments were completed, the sorbent columns were attached to the outlet of the soil columns to allow Hg containing soil column leachate to enter the sorbent columns. The initial breakthrough of both Hg and Br⁻ is presented as relative pore volumes so that their rates of elution can be directly compared to each other. The Br⁻

tracer is represented as relative concentration, i.e., the concentration of the tracer in the effluent over the initial concentration (C_{Eff}/C_{In}). We present the initial breakthrough of Hg and Br⁻ on the same figure to qualitatively compare Br⁻ and Hg breakthrough curves to each other.

Nonreactive Tracer Sample Analysis

Bromide concentrations were determined using a colorimetric assay (Lepore and Barak 2009). Two stock solutions were prepared; 2.45 mM chloramine trihydrate and 1.63 mM phenol red (Sigma Aldrich, St. Louis, MO, USA). A buffer stock was prepared consisting of 0.5 M of sodium acetate, 0.5 M of glacial acetic acid, and 12.3 mM of ammonium acetate and adjusted to a pH of 4.6. The buffer stock and phenol red stock solutions were mixed at a 1:1 (v/v) ratio immediately before use. In a 1.5-mL microcentrifuge tube, 870 μL of the Br⁻ standard or sample was added to 65 μL of the phenol red-buffer mixture, followed by the addition of 65 μL of chloramine trihydrate. The mixture was allowed to react at room temperature for 30 min in the centrifuge tube. The solution was then transferred to a 1-mL cuvette and the absorbance at 590 nm was recorded using a UV-Vis spectrophotometer (Figure 3). A calibration curve was created on a Cary UV-Vis spectrophotometer (Agilent Technologies, Inc., Santa Clara, CA) by preparing 5 stock solutions of Br⁻ in ACW to represent different concentrations at 1 ppm, 3 ppm, 5 ppm, 7 ppm and 10 ppm and a baseline correction prior to sample analysis with ACW solution.



Figure 3 - (left to right) – Agilent Cary UV-Vis Spectrophotometer, Tracer Test Samples Reacted with Colorimetric Assay Reagents

Pore Volume Calculations

Pore volumes were determined by weighing the mass of the sorbent within the column dry and then performing a displacement test for the volume. The length of the polycarbonate column was 9.2 cm and the radius was 2.0 cm. Final pore volumes are shown in Table 2.

Table 2 - Calculated pore volumes

Media	Pore Volume [mL]
Quartz Sand	13.02

Granular Activated Carbon	19.02
Biochar	12.70

Advective - Dispersive Transport Equation and Model Calculations

A numerical model simulation implemented in Python was used to describe the transport of a non-reactive tracer through a column (Lampert 2020). Data from non-reactive tracer experiments was used to determine several key solute transport parameters for each sorbent column (Table 3).

- Flow velocity (U): The velocity of the fluid in the column is an important parameter for determining the advection component of solute transport.
- Dispersion coefficient (D): The dispersion coefficient describes the spreading of the solute due to diffusion and other processes that lead to mixing in the fluid.

These parameters can be determined by monitoring the movement of a conservative tracer (e.g. Br^-) through the column and fitting the breakthrough curve (the concentration vs. time curve) obtained from the column experiment to the analytical solution of the ADE. Furthermore, the following additional parameters can be obtained:

- Retardation factor (R): The retardation factor is a measure of the extent to which the solute is retained in the porous medium due to sorption or other processes. It is defined as the ratio of the bulk fluid velocity to the effective velocity of the solute, which takes into account the rate of sorption.
- Porosity (Φ): The porosity of the porous medium is a measure of the fraction of the volume that is occupied by voids or pores.

Table 3 – Key parameters describing solute transport in the column

Parameter	Description
C_0	Solute influent concentration (M L^{-3})
U	Flow velocity in column (LT^{-1})
D	Dispersion coefficient (L^2T^{-1})
L	Length of column (L)

The model simulation calculates the concentration of the conservative tracer for different points in the column and generates a breakthrough curve. The parameters for the dispersion coefficient (D) and flow velocity (U) were iteratively adjusted to minimize the difference between experimental and calculated breakthrough curves.

The Python code was implemented in a Jupyter notebook within Anaconda, a distribution of the Python programming language for scientific computing (<https://anaconda.com/>). To run the simulation of the Br^- breakthrough curves, key Python libraries such as Pandas, Numpy, and Matplotlib were imported. Pandas was used for data import and analysis, NumPy for array calculations and mathematical functions, and Matplotlib for plotting the results.

Particle Retention Tests

The retention of particulates by quartz and sorbents was evaluated. Initial tests were performed using a suspension of zinc sulfide (ZnS) in ACW. The particle suspension was prepared using 15 mg of ZnS in 30 mL of ACW creating a 500 ppm ZnS stock. The stock suspension was transferred to a glass tube and sonicated for one hour until particles were properly dispersed throughout the solution. The stock solution was diluted to a final concentration 500 ppb ZnS in ACW. The ZnS suspension was constantly stirred and introduced to the quartz sand column at a flow rate of 1.0 mL/min. Effluent samples (4 mL each) were collected using the fraction collector and were analyzed using dynamic light scattering (DLS). After confirming the breakthrough of ZnS particles in the column effluents, additional experiments with mercury sulfide as metacinnabar (β -HgS) suspensions at concentrations of 1 ppm and 10 ppm were performed with identical preparation and experimental used for the ZnS suspension.

Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS), is a powerful tool for measuring size distributions of small particles in a solution. The intensity of scattered light from a dilute sample is measured as a function of time. A laser is used as a light source and the scattered light is collected at a fixed angle using a detector. The Brownian motion of the particles in the sample causes fluctuations in the intensity of the scattered light. The movement of the particles in the sample is characterized by the autocorrelation function of the scattered light intensity as a function of time. The autocorrelation function is analyzed using the Stokes-Einstein equation to determine the size distribution of the particles (Hassan, Rana et al. 2015).

Aliquots of 2 mL from the column effluents were taken at various time intervals, and then transferred to a cuvette to be measured on the on a Brookhaven 90Plus Particle Size Analyzer (Brookhaven Instruments Corp, Holtsville, NY, USA). The instrument uses a split laser beam configuration for automatic light intensity calibration, a photon-counting detector at a 90° degree angle to the incident beam. Autocorrelation profiles and average multimodal and log-normal size distributions from 10 individual measurements were recorded for each sample.

3. RESULTS AND DISCUSSION

Bromide Breakthrough Curves (Sand/GAC)

Tracer tests were conducted for columns with quartz sand and GAC. The concentration of the nonreactive tracer Br^- in the effluent (C_{eff}) was monitored relative to its concentration in the influent solution (C_{in}) for about 20 pore volumes. The breakthrough curve for the Br^- tracer in the quartz sand column is shown in Figure 4. As the tracer moves through the quartz sand, its concentration gradually increases until it reaches a peak value ($C_{\text{eff}}/C_{\text{in}} = 1$). At this point the concentration of the tracer has equilibrated with the porous medium. At 9.5 pore volumes the influent solution was switched back to ACW (no Br^-) and $C_{\text{eff}}/C_{\text{in}}$ was recorded until it effectively returned to zero.

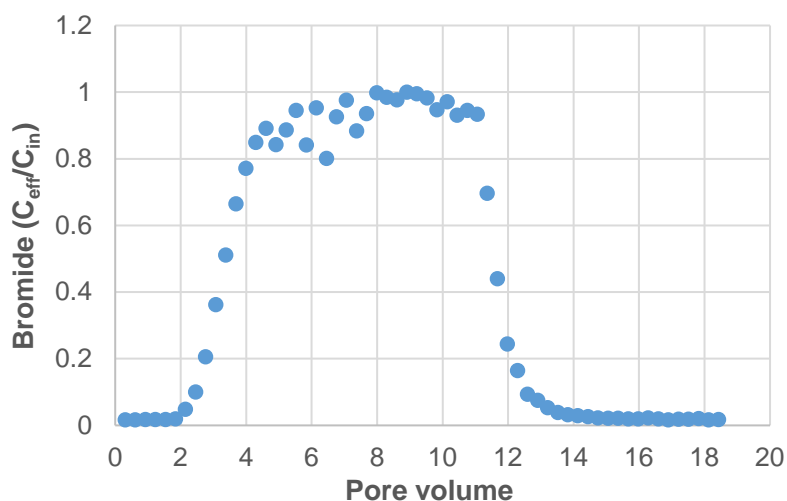


Figure 4 - Breakthrough curve of bromide in quartz sand column

In the breakthrough curve for the GAC sorbent column (Figure 5), equilibrium ($C_{\text{eff}}/C_{\text{in}} = 1$) was reached after approximately 20 pore volumes. At 25 pore volumes the influent solution was switched back to ACW (no Br^-) and $C_{\text{eff}}/C_{\text{in}}$ was recorded until it effectively returned to zero.

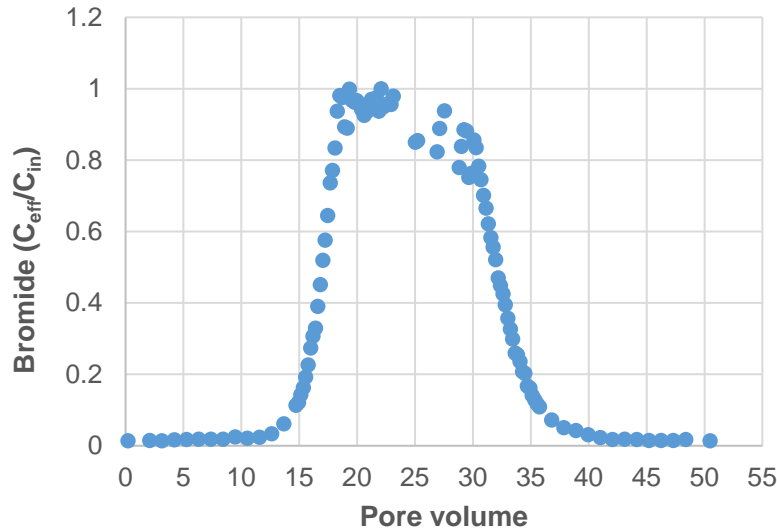


Figure 5 - Breakthrough Model of Bromide on GAC

Advection and Dispersion Graphs from Model Simulations

The breakthrough curve for the quartz sand column was simulated using the Python implementation of the ADE model to estimate the solute transport parameters (Table 3). The model parameters were iteratively fit to the concentrations of the Br⁻ tracer in the effluents. Figure 7 (left) shows the experimental data (dashed blue line), ideal plug flow model (blue dashed-dotted line) and the simulated breakthrough curve (red line). Figure 7 (right) shows the simulated evolution of the Br⁻ concentration profile over time throughout the length of the quartz sand column.

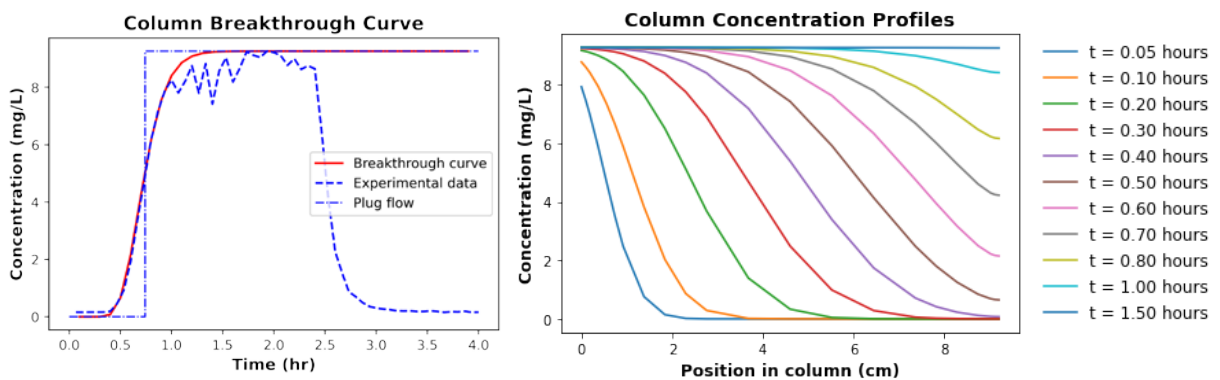


Figure 6 – Experimental and simulated for Br⁻ tracer in sand column

In addition, the breakthrough curve for the GAC sorbent column were simulated using the Python implementation of the ADE model to estimate the solute transport parameters (Table 3). The model parameters were iteratively fit to the concentrations of the Br⁻ tracer in the effluents. Figure 7 (left) shows the experimental data (dashed blue line), ideal plug flow model (blue dashed-dotted line)

and the simulated breakthrough curve (red line). Figure 7 (right) shows the simulated evolution of the Br^- concentration profile over time throughout the length of the GAC sorbent column.

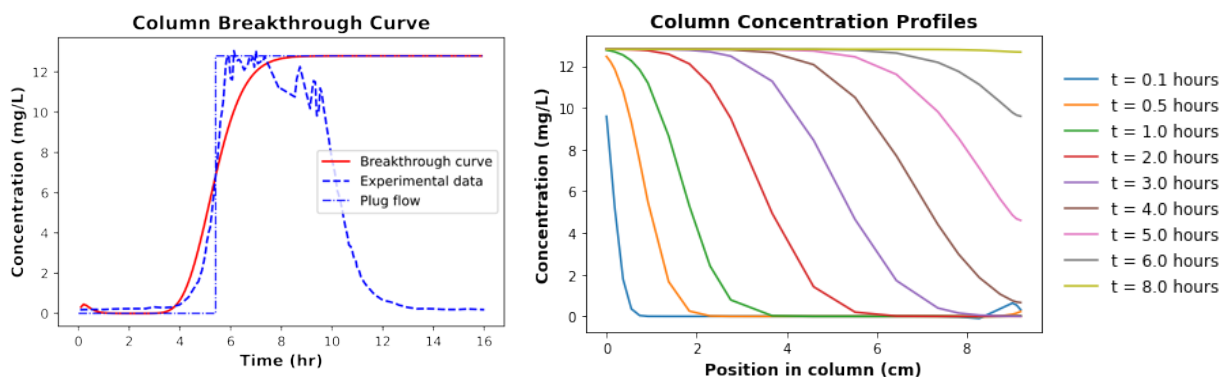


Figure 7 - Simulated GAC Br- Breakthrough on Python

Results from Particle Retention Experiments

The retention of particles on the quartz sand column was evaluated with influent solutions containing particles suspended in ACW. The influent solutions consisted of particle suspensions with broad size distributions ranging from colloidal particles (nm) to micron-sized particles (μm). Three different particle suspensions at different concentrations (500 ppb ZnS, 1 ppm HgS and 10 ppm HgS) were used for these experiments. Time-dependent changes in the particle size distributions in the effluents over time were determined. Samples of the effluent solutions were collected throughout each experiment and were analyzed using DLS.

The results from the three experiments consistently showed a linear increase of the mean particle diameter in the effluent. In the first experiment with the 500 ppb ZnS solution, the mean particle size increased from approximately 400 nm to 650 nm over a period of 2 hours (Figure 8). The second experiment with the 1 ppm HgS suspension as the influent resulted in an initial average effluent particle size of approximately 400 nm, which increased gradually to approximately 5 μm over a period of 5 hours (Figure 9). The third experiment with the 10 ppm HgS suspension showed an increase in the mean particle size from approximately 400 nm to 1.2 μm over a period of 6 hours (Figure 10).

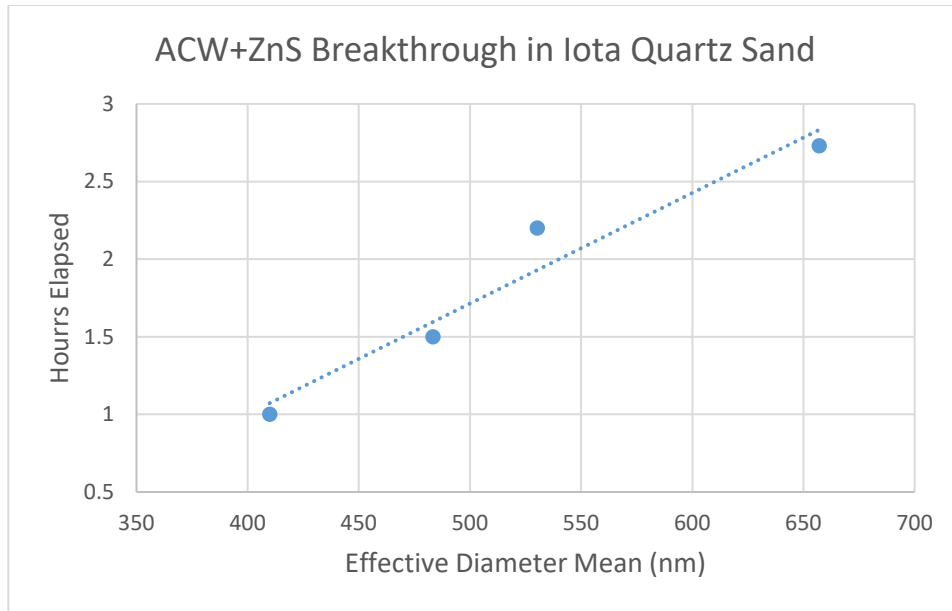


Figure 8 - ZnS (500 ppb) mean particle size change in column effluent

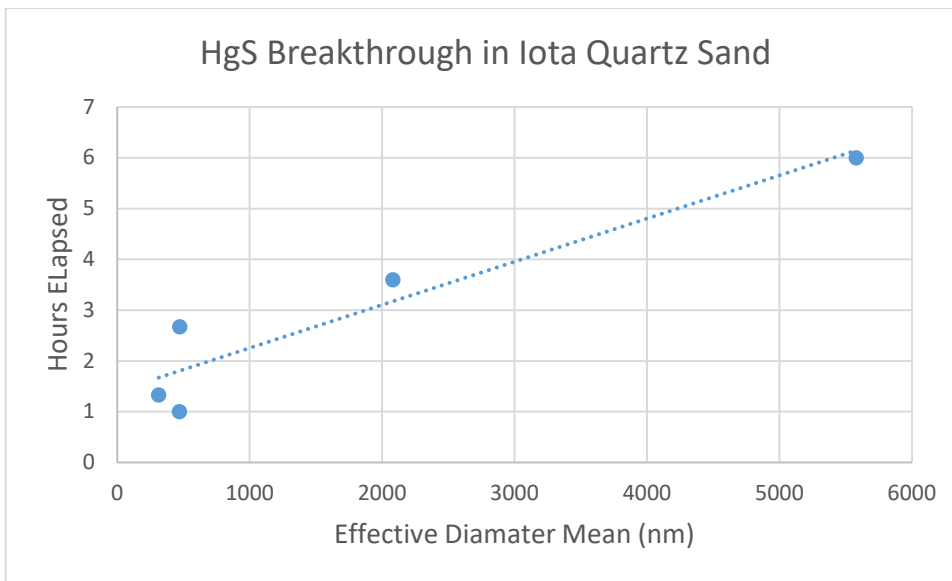


Figure 9 - HgS (1 mg/L) mean particle size change in column effluent

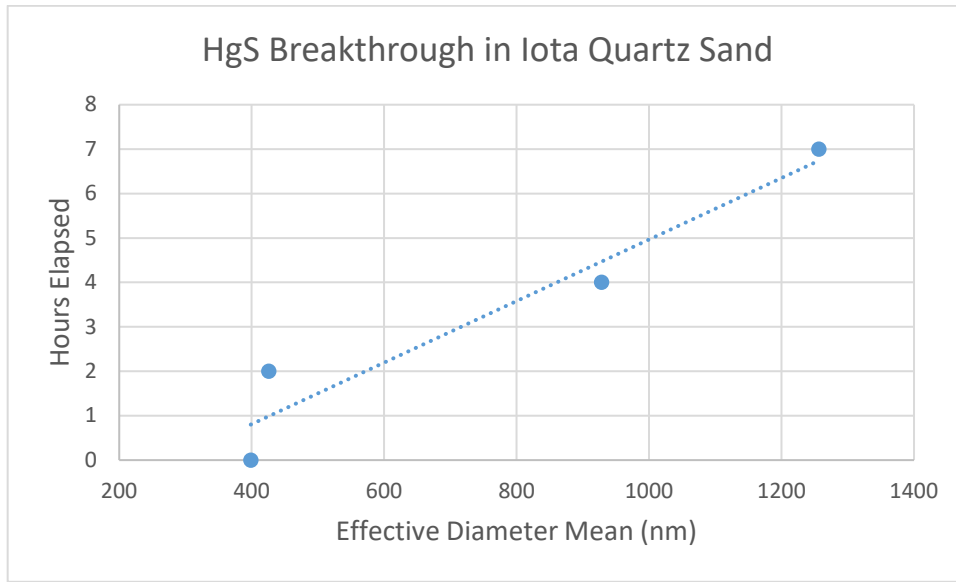


Figure 10 - HgS (10 mg/L) mean particle size change in column effluent

4. CONCLUSION

The results demonstrate the importance particulate retention by porous media such as quartz sand and engineered sorbents. Based on the data collected from the various column experiments, it can be concluded that particle sizes in the column effluents consistently increase over time. Further, experiments to determine the Hg concentration were inconclusive (data not shown), but for experiments with HgS it was observed that there is a correlation between mean particle size and Hg concentration in the column effluents. Further studies are needed to investigate and characterize particulate mercury mobilized from contaminated creek banks in LEFPC and how they are retained by sorbents. Moreover, the long-term stability of particulate Hg captured in a sorbent matrix needs to be determined as microbial activity and redox processes at the pore scale may mobilize Hg from sorbents. The results from this exploratory study show that engineered sorbents can retain particulate Hg, but future studies are needed to quantify the relative immobilized fractions of particulate and dissolved Hg species, respectively. The role particulate Hg species and their interactions with engineered sorbents will inform the design of effective remediation strategies for East Fork Poplar Creek.

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APPENDIX

Total Hg Analysis in Aqueous Samples Standard Operating Procedure

Sample preparation

1. Prepare a mercury blank by adding an aliquot of the Hg(II) stock to a BrCl solution in MQ water.
2. Dilute samples with MQ water as needed and add BrCl to the samples in clear glass vials (at least 1% or 50 μL BrCl for 5 mL of sample).
3. Let the BrCl-sample mixtures react overnight. The solution should turn clear, but a slight yellow tint indicating excess BrCl should remain. Sniff test (for the smell of BrCl) should indicate excess of BrCl in the samples. Should the color of the reaction mixture should turn from light yellow to colorless, add more BrCl and continue incubation for at least 6 hrs. Highly organic sample matrices, will require high levels of BrCl (e.g. 500 μL /10 mL of sample) and longer oxidation times.
4. For samples treated with BrCl, add 25 μL of 30% (w/v) hydroxylamine solution per 100 μL BrCl of sample, mix well and allow sample to react for 5 minutes (yellow color should disappear).

Reagent Recipes

- a. Bromine monochloride (BrCl): Dissolve 27 g of trace metal grade potassium bromide (KBr) in a 2.5 L bottle of concentrated HCl. Place a Teflon coated stir bar into the bottle and stir for 1 hour. Slowly add 38 g trace metal grade potassium bromate (KBrO_3) to the bottle while stirring. CAUTION: This needs to be done slowly and in a fume hood because large quantities of free halogens are produced. As KBrO_3 is added to the solution, the color should change from yellow to red to orange. Cap bottle loosely and allow stirring for an additional hour. The BrCl is analyzed for residual Hg prior to use. BrCl solution can be obtained from lab 259.
- b. 20% (w/v) stannous chloride (SnCl_2) stock: Add 100 g SnCl_2 to 50 mL concentrated HCl (trace metal grade) in a 500 mL bottle. Add 450 mL MQ water. Purge for 1 hour with ultrahigh purity N_2 . Prepare fresh every 6 months.
- c. 30% (w/v) hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) stock: Dissolve 30 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in a bottle containing 100 mL of MQ water. Add 100 μL stannous chloride stock solution and purge solution with ultrahigh purity N_2 for 1 hour to remove residual mercury. Prepare fresh every 6 months.

Reagent blanks are required when a new batch of reagents (bromine monochloride and hydroxylamine hydrochloride) are prepared. The amount of Hg in a reagent blank containing 0.5% (v/v) BrCl solution and 0.2% (v/v) hydroxylamine hydrochloride solution must be < 20 pg (0.2 ng/L).

The presence of more than 20 pg (0.2 ng/L) of Hg indicates a problem with the reagent solution. The purging of certain reagent solutions, such as SnCl_2 or NH_2OH , with mercury-free nitrogen or argon can reduce Hg to acceptable levels. Because BrCl cannot be purified, a new batch must be prepared and tested if the BrCl is contaminated.

Analysis (based on EPA method 1631)

- 2.1 Power on Lumex RA-915+ mercury analyzer and push the lamp start button for 2-3 seconds on the instrument. The instrument must be turned on **30 minutes prior to analysis** to allow the lamp output to stabilize.

- 2.2 Open software to ensure ignition of lamp. A low radiation error will appear if the lamp has not been lit.
- 2.3 Open vacuum valve on bench nozzle. Adjust flowmeter reading to approximately 1.0. Record beginning vacuum flow reading.
- 2.4 Turn on nitrogen gas: open regulator on tank and in-line benchtop valve. Note regulator pressures, **making sure N₂ cylinder is not close to empty**. Ensure gas flow from regulator and in instrument apparatus. After opening black benchtop N₂ valve, flowmeter reading will be between 1.0 and 1.3.
- 2.5 Prepare a set of fresh 0.8% (w/v) stannous chloride (SnCl₂) reagent solutions in 40 mL clear glass vials: Add 200 µl of the 20% (w/v) stannous chloride stock solution to approximately 5 mL of MQ water. The stannous chloride reagent solution should be changed after every 5 samples, if the volume in the vial exceeds 15 mL or if the calibration verification fails.
- 2.6 Prepare a 10 ppb Hg(II) standard. Add 4.9 mL of MQ water, 50 µl BrCl and 50 µl of 1 ppm Hg(NO₃)₂ standard solution to 40 mL amber glass vial. Ensure Hg stock is at room temp before pipetting. **Ensure Hg stock standard solution and samples do not come in contact with SnCl₂ before analysis!**
- 2.7 Open the RA-915P software and select Liquid mode from the main menu. Verify that the multipath cell mode is selected in the control toolbar. Monitor baseline approximately 120 seconds, then click Run in the graph toolbar. Perform baseline check for approximately 20 seconds. Click button again to set baseline. If baseline drift is observed, check tubing and soda lime for water accumulation.
- 2.8 Perform calibration using 10 µl, 20 µl, 50 µl, 100 µl, 200 µl volumes of 10 ppb Hg standard (corresponds to 0.1 ng, 0.2 ng, 0.5 ng, 1 ng, 2.0 ng Hg). R² of the linear regression for standards must be greater than 0.99. Run continuing calibration verifications (CCVs) (20 µL of 10 ppb Hg standard) every eight samples.
- 2.9 Add the required volume of standard or sample to reaction vial containing 0.8% (w/v) stannous chloride solution. Do not allow added standard or sample volume to come in contact with lines inside reaction vial or walls of reaction vial. Cap reaction vial as quickly as possible to prevent sample loss.
- 2.10 Close vial and immediately open N₂ valves on reaction vial and moisture trap in order. Press Start in the control software dialog box. Check gas flow on the flowmeter. Stop run after signal reaches the baseline (check dialog box) and record sample ID, added volume and peak area value in a spreadsheet. Results should also be recorded in a lab notebook. When analyzing a new sample **make sure to open vial before closing the gas line**. Change pipette tip after each sample to avoid contamination. Naming convention for saving spreadsheets: YYYYMMDD_Initials_Project_Description
- 2.11 Replace reaction vial with 0.8% (w/v) SnCl₂ after every five samples. Inspect tubing for moisture accumulation. If moisture is visible in tubing, purge with nitrogen gas and replace soda lime (4 – 8 mesh) in trap.
- 2.13 Monitor peaks for accurate shapes. If peak broadening occurs due to carryover or a visible film develops in trap vial, rinse organics from gas lines using 20% acetone and replace trap vial.
- 2.14 Remove organics from gas lines after each session with 20% acetone. Replace trap vial.
- 2.15 Close software and turn off Lumex.