

Black Carbon-Amended Engineered Media Filters for Improved Treatment of Stormwater Runoff

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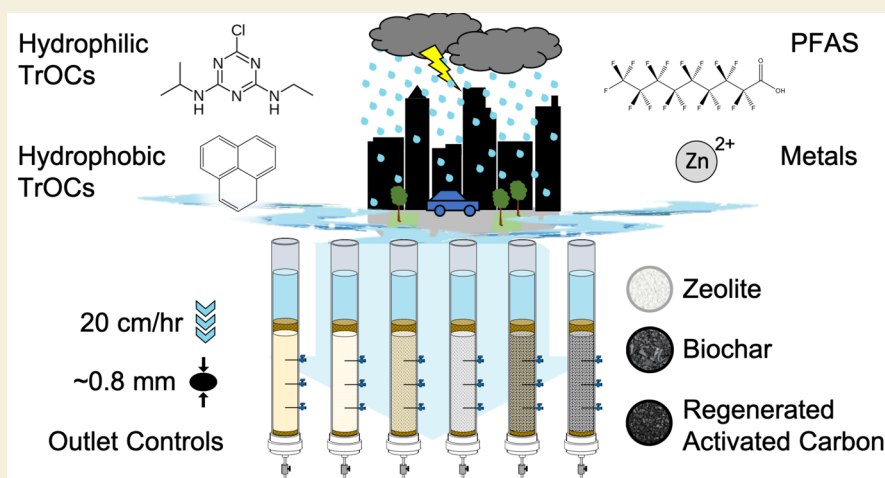
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ABSTRACT: Urban stormwater runoff is a significant driver of surface water quality impairment. Recently, attention has been drawn to potential beneficial use of urban stormwater runoff, including augmenting drinking water supply in water-stressed areas. However, beneficial use relies on improved treatment of stormwater runoff to remove mobile dissolved metals and trace organic contaminants (TrOCs). This study assesses six engineered media mixtures consisting of sand, zeolite, high-temperature gasification biochar, and regenerated activated carbon (RAC) for removing a suite of co-contaminants comprising five metals, three herbicides, four pesticides, a corrosion inhibitor, six per- and polyfluoroalkyl substances (PFASs), five polychlorinated biphenyls (PCBs), and six polycyclic aromatic hydrocarbons (PAHs). This long-term laboratory-scale column study uses a novel approach to generate reproducible synthetic stormwater that incorporates catch basin material and straw-derived dissolved organic carbon. Higher flow conditions (20 cm hr^{-1}), larger sized media (0.42–1.68 mm), and downflow configuration with outlet control increase the relevance of this study to better enable implementation in the field. Biochar- and RAC-amended engineered media filters removed nearly all of the TrOCs in the effluent over the course of three months of continuous flow (480 empty bed volumes), while sample ports spaced at 25% and 50% along the column depth provide windows to observe contaminant transport. Biochar provided greater benefit to TrOC removal than RAC on a mass basis. This study used relatively high concentrations of contaminants and low biochar and RAC content to observe contaminant transport. Performance in the field is likely to be significantly better with higher biochar- and RAC-content filters and lower ambient stormwater contaminant concentrations. This study provides proof-of-concept for biochar- and RAC-amended engineered media filters operated at a flow rate of 20 cm hr^{-1} for removing dissolved TrOCs and metals and offers insights on the performance of biochar and RAC for improved stormwater treatment and field trials.

KEYWORDS: Stormwater Runoff, Biochar, Regenerated Activated Carbon, Zeolite, Sorption, PFASs, Trace Organic Contaminants

INTRODUCTION

Urban stormwater runoff transports harmful contaminants to receiving waters and aquatic sediment. Global climate change and increased urbanization are expected to heighten the threat of stormwater runoff contamination because of increases in the intensity of storm events and growth of urban impervious surface area.^{1,2} Stormwater runoff is also a concern at military

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and industrial facilities because of the potential transport of contaminants off-site and recontamination of sediments following remediation efforts.³ The potential to augment drinking water supplies with urban stormwater runoff through managed aquifer recharge has also received increased attention in arid regions,⁴ though this recharge is dependent on improving water quality to avoid introducing contaminants into drinking water aquifers.⁵ Effective and efficient treatment of stormwater runoff entering receiving waters and underground aquifers is therefore necessary for both protection of human and aquatic health and augmentation of urban water supplies.

Urban stormwater runoff contains a variety of contaminants ranging from traditional water quality indicators such as total suspended solids (TSS) and turbidity to nutrients, pathogens, metals, and chemicals.^{6,7} Stormwater runoff is a significant mechanism for carrying metals such as cadmium, copper, lead, nickel, and zinc to receiving water bodies.⁸ In addition, many trace organic contaminants (TrOCs) are found in urban stormwater, including insecticides, herbicides, flame retardants, corrosion inhibitors, plasticizers, and legacy contaminants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). Hydrophilic organic contaminants are of particular interest because of their mobility and ubiquitous presence in stormwater, often at the ng L^{-1} to $\mu\text{g L}^{-1}$ range.⁹ Per- and polyfluoroalkyl substances (PFASs) continue to garner increasing attention because of their highly mobile and persistent nature. PFASs are reported in stormwater runoff and are a threat to drinking water supplies.¹⁰

Traditional stormwater control measures (SCMs) include grass swales, infiltration trenches, bioretention basins, and detention ponds. These measures focus primarily on depressing the storm hydrograph so as to return site hydrology to that of its predeveloped condition with the secondary goal of improving traditional water quality indicators such as TSS, turbidity, and fecal indicators through suspended particle removal.^{11–13} However, dissolved constituents such as hydrophilic TrOCs, PFASs, and metals pass through traditional stormwater control measures, posing risks downstream.⁶ Moreover, some hydrophobic TrOCs such as the pyrethroid bifenthrin are observed in stormwater runoff in the dissolved phase at greater concentrations than expected based solely on their equilibrium partitioning coefficients, indicating that hydrophobic TrOCs may not be removed completely by suspended particle removal.¹⁴

Past studies have investigated improved treatment of urban stormwater runoff using engineered media amendments to remove nutrients and organic, metallic, and microbial contaminants.⁶ Specifically, black carbonaceous matter (black carbon, BC) such as activated carbon and biochar show promise for reducing these contaminants.^{15–21} Activated carbon (AC) is produced from coal, coconut husks, and peat by pyrolytic carbonization and subsequent activation by steam at 850–1200 °C.²² Regenerated activated carbon (RAC) is produced by thermal regeneration and reactivation of spent activated carbon. Biochar is a lower-cost alternative (350–1200 \$ metric ton⁻¹) relative to activated carbon (1100–1700 \$ metric ton⁻¹).²³ Biochar consists of organic material, often wood, agricultural, or other waste, that has undergone pyrolysis or gasification. This entails the thermal decomposition of the volatile compounds of an organic substance when heated (350–600 °C for pyrolysis; 800–1200 °C for gasification) in the absence of oxygen.²⁴ Biochar is desirable because of its

high surface area ($\sim 300\text{--}600 \text{ m}^2 \text{ g}^{-1}$), though less than that of AC ($\sim 900\text{--}1000 \text{ m}^2 \text{ g}^{-1}$).^{19,22} Biochar performance is highly variable based on feedstock material and production process, with higher-temperature biochars exhibiting more favorable TrOC removal while lower-temperature biochars, which often contain increased number of polar functional groups on the biochar's surface, have inconsistent performance depending on material and manufacturing conditions.^{25,26} Additionally, low-cost mineral sorbents such as natural zeolites show potential for removing nutrients and metals from environmental flows.²⁷ Zeolites are crystalline hydrated aluminosilicates with high surface area ($30\text{--}180 \text{ m}^2 \text{ g}^{-1}$) and negative surface charge that are a naturally occurring mineral in basaltic lava.^{28–30} Predominant removal mechanisms of zeolite include sequestration, adsorption, and cation exchange, of which the exchangeable ions are Na^+ , Ca^{2+} , and Mg^{2+} .³¹

Past studies on use of BC such as biochar or AC for stormwater treatment have investigated a limited range of conditions, including low flow rates, relatively fine particle sizes, and few co-contaminants.^{15–20,32} As reported in Table 1,

Table 1. Conditions of Previous Studies on TrOC Removal in BC-Amended Filters

study	flow rate	particle size	materials ^a
Ashoori et al., 2019 ¹⁶	1.5 cm hr ⁻¹	>600 μm	MCG-biochar, 33 wt %
Cederlund et al., 2017 ¹⁷	2.4 cm hr ⁻¹	<2 mm	W-biochar, 1.25–10 cm layer
Portmann et al., 2022 ³⁵	2.6 cm hr ⁻¹	53–250 μm	MCG-biochar, 0.5 wt %
Ray et al., 2019 ¹⁵	12 cm hr ⁻¹	100–300 μm	MCG-biochar, 3 wt %
Spahr et al., 2022 ²⁶	9 cm hr ⁻¹	595–841 μm	MCG-biochar, 0.87 wt %
Sun et al., 2020 ¹⁸	6.1 cm hr ⁻¹	<1.8 mm	SAW-biochar, 5 wt %
Ulrich et al., 2015 ¹⁹	5.3 cm hr ⁻¹	53–264 μm	F300-AC, 0.4 wt %; MCG-biochar, 0.2 wt %; BN-biochar, 1.0 wt %
Ulrich et al., 2017 ²⁰	2.6 cm hr ⁻¹	53–250 μm	MCG-biochar, 0.5 wt %

^aMCG, Mountain Crest Gardens, CA; W, wood-based; SAW, sulfuric acid-treated wood-based; BN, Biochar Now, CO.

recent studies have employed low flow rates of several cm hr^{-1} and grain sizes typically less than 800 μm . Slow treatment flow rates would require larger SCM foot prints to hold and treat all of the stormwater runoff and are not necessarily representative of typical design guidance which specifies infiltration rates in the range of 7–22 cm hr^{-1} for stormwater runoff treatment.^{33,34} Increasing the flow rate necessitates increased particle sizes to facilitate hydraulic conductivity and results in shorter contact times, both of which are expected to negatively affect contaminant removal kinetics. Additionally, increasing the number of co-contaminants may also reduce the filter's performance for individual contaminants.²⁵ Investigating more realistic flow rates, coarser media sizes, and increased presence of co-contaminants was incorporated into this study to investigate the limits of filter performance and understand the real-world relevancy of BC-amended technologies. Such work will inform throughput-performance trade-offs and design choices.

This study investigated six engineered media mixtures and offers proof-of-concept for effective and efficient high-

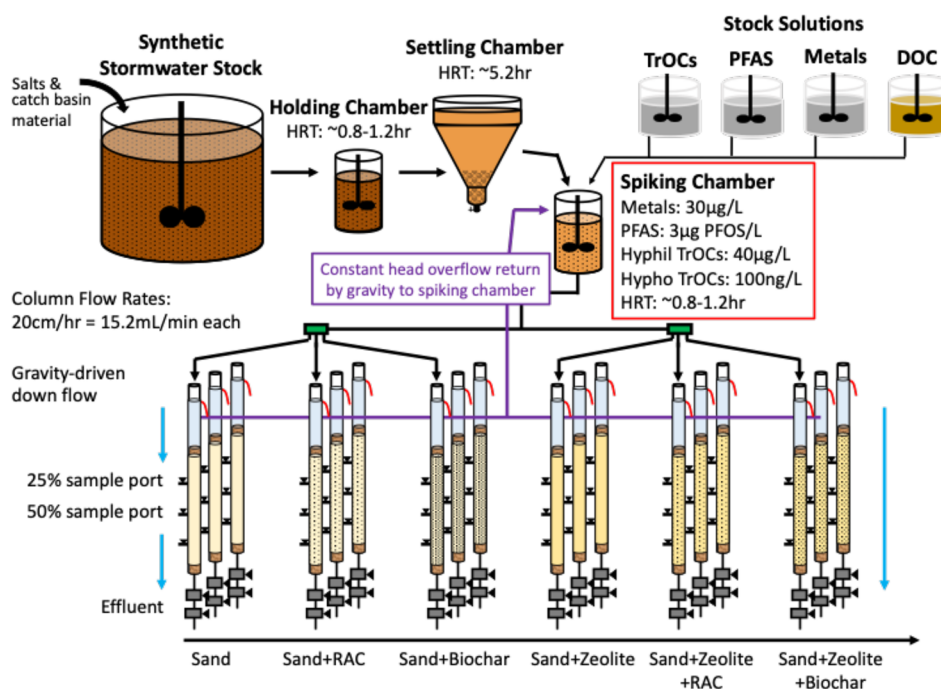


Figure 1. Diagram of experimental setup showing the stormwater generation, contaminant spiking, and treatment columns. Constant head was maintained in the columns by continuous overflow back to the spiking chamber. System details may be found in Tables A.9 and A.11 and Figure A.21.

throughput treatment of stormwater runoff for a wide range of contaminants by BC-amended engineered media filters. Six mixtures of sand, zeolite, biochar, and RAC were investigated for contaminant removal at the laboratory scale using a novel synthetic stormwater and down-flow configuration with outlet controls to maintain the treatment flow rate. Particle size of 420 μm to 1.68 mm (12–40 mesh) and a face velocity of 20 cm hr^{-1} were used to facilitate the direct transfer of these studies to the field and thereby increase the relevancy of the findings. Furthermore, all materials used in this study are commercially available at scale.

MATERIAL AND METHODS

Synthetic Stormwater

This study builds on past procedures³⁰ for creating synthetic stormwater by using catch basin material from a US Department of Defense (DoD) facility to provide a background matrix of ions, dissolved organic carbon (DOC), and microbial community inoculum. Materials from US Navy and Air Force sites were evaluated, and catch basin material from Naval Weapons Station Seal Beach (NWSSB), CA, USA was selected for use in the long-term tests based on material availability, contaminant content, and DOC leaching. Catch basin material was collected from stormwater drains from parking lots near a wash station and wharf area, screened with 3 mm mesh to remove debris and trash, and homogenized. Catch basin material and salts were mixed into deionized (DI) water to create a base synthetic stormwater. The recipe is summarized in the Supporting Information (Table A.1). Suspended solids were removed from the synthetic stormwater using a sedimentation tank with a hydraulic residence time of 5.2 h, as is typical of pretreatment systems used in many SCMs. Additional DOC concentrate derived from straw was added to the synthetic stormwater to reach an environmentally relevant DOC concentration. The DOC concentrate was created by soaking straw (construction site straw wattle, Home Depot, CA) in DI water for 3 days, filtering with a 400 mesh sieve (38 μm), autoclaving, and freezing at $-20\text{ }^{\circ}\text{C}$ until use. Straw was chosen because it is

known to release high amounts of DOC and was found in the catch basin material received from NWSSB.

Filter Engineered Media

Biochar Supreme (Environmental Ultra; Everson, WA, USA), Cabot Corporation regenerated activated carbon (830R; Alpharetta, GA, USA), and BioGreen Technologies zeolite (Boulder, CO, USA) were selected for evaluation based on literature and preliminary batch sorption experiments (Figures A.12 and A.13). Sand (Cemex, Lapis Luster 12/20; Houston, TX, USA) and barrier sand (Cemex, Lapis Luster 6 \times 12; Houston, TX, USA) were locally obtained (Peninsula Building Materials, Redwood City, CA, USA). Materials were received dry and sieved to 1.68 mm to 400 μm (12–40 mesh) using a motorized sieve shaker (Humboldt H-4330; Elgin, IL, USA). Particle size analysis was conducted on the sieved materials by dry sieving. Barrier sand was used as received without sieving. All materials are currently commercially available at scale. Black carbon materials were characterized for pore size distribution using Mercury Intrusion Porosimetry (MIP) analysis (Particle Technology Laboratories; Downers Grove, IL, USA).

Chemicals

The study was designed to evaluate the removal of hydrophilic trace organic chemicals at a nominal concentration of about 40 $\mu\text{g L}^{-1}$, hydrophobic organic chemicals at 0.1 $\mu\text{g L}^{-1}$, and aqueous film-forming foam (AFFF)-derived PFASs at 3 $\mu\text{g PFOS L}^{-1}$. Chemicals were ordered as neat analytical standards and used as received. All solvents used were analytical grade quality. Primary stock solutions for the hydrophilic (hyphil)- (benzotriazole, atrazine, diuron, imidacloprid, fipronil, and mecoprop) and hydrophobic (hypho)-TrOCs were made in methanol and hexane, respectively. A plating technique was used to create a secondary stock solution (1.6 mg L^{-1}) devoid of solvent by adding primary stock solutions to a glass jar, allowing the solvent to evaporate, adding DI water, and sonicating (Creworks, TRTV1847; Lake Forest, CA, USA) the solution for 1.5 h to ensure dissolution of the solutes. A previously characterized³⁶ sample of an AFFF (3M, Minneapolis, MN, USA) concentrate primarily containing electrochemical fluorination-produced PFASs was obtained from a U.S. Air Force base storage tank and used to deliver a representative

Table 2. Measured Column Porosity, Contact Time, and Hydraulic Conductivity

eng. media mixture	BC content		porosity ^a	nominal contact time ^b [min]	hydraulic conductivity [cm s ⁻¹] ^c	
	vol %	wt %			initial	<i>t</i> = 62 days
sand			0.30 ± 0.03	54	0.69 ± 0.22	0.35 ± 0.04
+ zeolite			0.42 ± 0.01	76	0.50 ± 0.07	0.37 ± 0.01
+ RAC	10	3.3	0.37 ± 0.01	67	0.42 ± 0.02	0.31 ± 0.03
+ biochar	30	2.4	0.51 ± 0.05	92	0.31 ± 0.01	0.21 ± 0.08
+ zeolite + biochar	30	3.0	0.60 ± 0.01	108	0.47 ± 0.08	0.28 ± 0.08
+ zeolite + RAC	10	4.0	0.44 ± 0.00	79	0.44 ± 0.00	0.33 ± 0.04

^aMeasured gravimetrically using dry and saturated weights. Average ± standard deviation (*n* = 3). ^bComputed based on measured porosity and flow rate. Note, empty bed contact time (EBCT) = 3 h. ^cInitial hydraulic conductivity tested after flushing with DI water but before conditioning. Average ± standard deviation (*n* = 3).

mixture of PFASs by diluting into MTBE such that the final concentration of MTBE in the secondary stock was <0.25 vol %, and <0.0031 vol % in the spiked synthetic stormwater (see Table A.5 for details).

Column Experiments

Figure 1 is a diagram of the experimental setup. Engineered media mixtures consisting of sand amended with zeolite (30 vol %), biochar (30 vol %), and regenerated activated carbon (10 vol %) were tested in triplicate. Low weight percent sorbents, 2.4 wt % biochar and 3.3 wt % RAC, were employed in order to observe transport of TrOCs during the experiment (Table 2). Columns (1.22 m length, 7.6 cm inner diameter) were constructed of clear PVC with a sufficient size ratio (column diameter to maximum grain diameter) to ensure proper fluid hydraulics.³⁷ Premeasured masses of engineered media were mixed dry by hand. The columns were filled with 10 cm of barrier sand followed by 60 cm of engineered media followed by 6 cm of barrier sand on top. A mechanical massager was used to ensure adequate packing of the material and column, and ~4 cm lifts of material were massed to ensure proper distribution of engineered media amendments vertically in the column. The columns were then saturated in an up-flow configuration with carbon dioxide gas for 1 h at a flow rate of 2 L min⁻¹ and then with DI water at a flow rate of 3.4 mL min⁻¹. Carbon dioxide gas was used to displace the air inside the column and grains because it dissolves readily in water. The columns were then flushed with DI water in the downflow configuration, and outlet controls were used to control the flow rate of 20 cm hr⁻¹ (15.2 mL min⁻¹). Tracer tests were conducted using bromide as a conservative tracer (Figure A.22); the porosity was determined gravimetrically. During the tracer test, the water level in the columns was reduced to the top of the barrier sand to prevent initial dilution of the tracer. The columns were then conditioned with synthetic stormwater for 100 empty bed volumes (EBVs). Finally, the columns were challenge-tested with synthetic stormwater spiked with contaminants for about 480 EBVs. Constant head (~39 cm) was maintained in the columns by continuous overflow of water back to the spike tank, as shown in Figure 1.

During the conditioning and challenge tests, synthetic stormwater and contaminant stock solutions were prepared every 2–3 days. Synthetic stormwater was made periodically, and DOC, total nitrogen, and other water quality parameters were measured periodically to ensure consistent quality over the course of the experiment. Contaminants were spiked at various concentrations, as shown in Figure 1, to ensure adequate detection within 2 orders of magnitude change in concentration. Following the challenge tests, the columns were flushed with ~40 EBVs of synthetic stormwater. The flow rate of each column was checked daily and adjusted to maintain the target flow rate. Every 6–8 days, tubing, tanks, and the barrier sand on top of the columns were cleaned to remove biological growth. The hydraulic conductivity was monitored throughout the experiment using manometers attached to the 25% and 75% sample ports. Detailed system information is shown in the Supporting Information.

Isotherm Measurements. Batch isotherms were conducted for the hydrophilic TrOCs for the biochar and RAC. Experiments were conducted by adding increasing amounts of biochar (10 mg L⁻¹ to

250 mg L⁻¹), RAC (10 mg L⁻¹ to 380 mg L⁻¹), and sodium azide (200 mg L⁻¹) to 15 L amber jars. Sodium azide was used to inhibit biological growth, as commonly used in the past.¹⁹ Synthetic stormwater with 9.5 ± 0.7 mg C L⁻¹ DOC was then added, and the jars were spiked with all the contaminants together. The samples were placed onto a horizontal shaker for 90 days. Initial contaminant concentrations were increased by a factor of 2.5 from levels used in the column experiment to 100 μg L⁻¹ hyphil-TrOCs, 250 ng L⁻¹ hypoph-TrOCs, 900 μg L⁻¹ metals, and 8 μg PFOS L⁻¹ PFAS to increase the range of detection, as was necessary because of the large range in contaminant sorption properties. Fifteen distinct masses of each black carbon were added to jars in order to capture the wide range in compound sorption parameters. Synthetic stormwater was generated with the same recipe as used in the column experiments, with a background level of DOC as was used in the column experiment.

Analytical Methods

Water samples were collected from the influent, the 25% and 50% sample ports, and column effluent in 20 mL glass vials (hyphil-TrOCs), HDPE 20 mL vials (metals, DOC), 15 mL polypropylene centrifuge tubes (PFASs) and frozen at -20 °C until analysis. Hyphil-TrOC samples were filtered using 0.45 μm glass fiber syringe filters (SF15159, Tisch Scientific, OH, USA), transferred to 2 mL glass vials, spiked with internal standards, and analyzed using liquid chromatography with tandem mass spectrometry (LC-MS/MS, API 3000; Applied Biosystems, Waltham, MA, USA). Additional details are provided in the Supporting Information. Metal samples were filtered using 0.45 μm PES syringe filters (SF14501, Tisch Scientific, OH, USA), transferred to 15 mL Falcon tubes, spiked with 300 μL of concentrated nitric acid, and analyzed using inductively coupled plasma mass spectrometry (ICP-MS). PFASs were analyzed via direct injection on a LC-QToF-MS instrument (X500R; SCIEX, Framingham, MA) operated in negative electrospray mode.³⁸ Only quantitative targeted PFAS analyses are reported here.

Hydrophobic-TrOC (hypoph-TrOC) samples were collected from the influent and effluent in 1 L amber glass jars and immediately filtered using a vacuum filter assembly and 1.6 μm glass fiber filters (28497-153, Whatman grade GF/A). The filters were dried at 60 °C, weighed, and frozen at -20 °C until analysis. The filtrate was promptly extracted using dichloromethane (DCM) similar to EPA Method 3510 C. Surrogate standards and sodium chloride were added, and the samples were transferred to 2 L separatory flasks. 40 mL of DCM was added, and the samples shaken vigorously for 30 s. The DCM was allowed to separate with the aid of heat and collected, and the extraction was repeated two additional times. Sodium sulfate was added to the collected DCM to remove water, and the DCM was concentrated to about 10 mL using a roto-vap. The extracted samples were then solvent transferred to hexane and cleaned up using silica SPE cartridges and sodium sulfate. Finally, the solvent sample was evaporated to about 1 mL under nitrogen, internal standards were added, and the sample analyzed using gas chromatography with mass spectrometry (GC-MS). Additional details are provided in the Supporting Information.

Table 3. Comparison of Empty Bed Volumes Treated for Dissolved Metals as Indicated by $C/C_0 = 0.4$ at the Column Effluent

eng. media mix	EBVs treated until $C/C_0 = 0.4$ at column effluent ^b											
	Al		Ni		Cu		Zn		Cd		Pb	
sand	26	±1	35	±13	25	±2	26	±1	74	±5	>450	– ^c
+ zeolite	60	±3	72	±1	59	±28	60	±3	164	±2	>450	–
+ RAC	122	±35	275	– ^c	44	±42	122	±35	237	±41	>450	–
+ biochar	76	±2	>450	–	38	±30	76	±2	129	±35	>450	–
+ zeolite + biochar	124	±39	>450	–	39	±43	124	±39	201	±4	>450	–
+ zeolite + RAC	172	±18	>450	–	105	±94	172	±18	213	±16	>450	–
inf. conc. ^a [ug/L]	17.6	±2.2	16.8	±1.9	20.2	±7.9	17.6	±2.2	8.8	±2.7	1.1	±0.6

^aTime weighted average ± standard deviation ($n = 3$). ^bMean ± standard deviation ($n = 3$) [EBVs]. ^c– Indicates no calculated value because of lack of observed contaminants in sample.

Dissolved oxygen (DO) was measured with a YSI ProODO probe (YSI Inc., Yellow Springs, OH, USA) in the column effluent using a flow-through cell to prevent O₂ contamination from the atmosphere. pH, electrical conductivity, total dissolved solids (TDS), and temperature were measured with a portable Ultrameter II 6P multiparameter probe (Myron L Company, Carlsbad, USA). DOC was analyzed after filtration (0.45 μm PES) using a TOC analyzer (Shimadzu TOC-VCSH). TSS was calculated by weighing the mass of sediment retained on 1.6 μm glass fiber filters using a vacuum filter assembly.

RESULTS AND DISCUSSION

Basic Water Quality Parameters and Hydraulic Conductivity

The columns were conditioned and challenge-tested with synthetic stormwater prepared as described above using catch basin material from Naval Weapons Station, Seal Beach, CA (NWSSB). TSS ranged from 13.5 to 40.2 mg L⁻¹ in the column influent, and turbidity averaged 181 ± 109 FNU presedimentation and 26.9 ± 3.9 FNU in the column influent. All treatments provided substantial water quality improvement with respect to TSS and turbidity (Figures A.25 and A.29). TSS was removed to 0.0–1.3 mg L⁻¹ at the effluent (97–99%), although the columns amended with BC consistently removed more TSS. Zeolite amendment did not significantly improve TSS removal. Similar trends were observed for turbidity, which ranged from 0.48 to 2.22 FNU in the column effluent. Biochar amendment reduced the turbidity the most (0.76 ± 0.16 FNU, 97% removal), followed by RAC amendment (1.33 ± 0.41 FNU, 95%). Zeolite amendment did not contribute to turbidity removal.

DOC was dosed to attain approximately 10 mg C L⁻¹ in the spiking chamber, and 3.7 ± 1.1 mg C L⁻¹ was present in the stormwater entering the columns. This difference is likely due to sorption to TSS and microbial degradation in the spiking chamber and tubing (Figure A.26), as there was substantial biomass accumulation in the spiking chamber and tubing downstream of the spiking chamber. Observed SUVA values of 2.59 L mg⁻¹ m⁻¹ in the synthetic stormwater influent are within the range typical of stormwater runoff.^{39,40} DOC was partially removed by all of the columns throughout the experiment in the order of RAC > biochar > sand ~ zeolite. While RAC and biochar amendment both reduced DOC similarly in the beginning (~80% at 120 EBVs); after ~200 EBVs, the DOC removal in the biochar decreased similar to the sand and zeolite columns (~55% at 208 EBVs) while DOC in the RAC columns remained at 70% at 208 EBVs. Zeolite did not impact DOC removal. The sand columns reduced the DOC by ~20% initially but steadily increased the removal to

~40% by the conclusion of the experiment. DOC removal in the sand columns is likely due to DOC capture with suspended solids initially and then gradually increased owing to biological degradation of the DOC until steady state. The DOC breakthrough profile (Figure A.26) in the biochar and RAC columns suggest that the primary mechanism for DOC removal is adsorption onto BC, as DOC was reduced completely at the beginning of the experiment before leveling off at ~70% removal because of saturation of surface DOC sorption sites on the BC. Total nitrogen remained fairly consistent in the column influent and was removed in the BC-amended columns by ~30%. Zeolite did not benefit total nitrogen removal.

Dissolved oxygen (DO), pH, electrical conductivity, and total dissolved solids trends were consistent throughout the experiment. The DO was depleted in all the columns during the conditioning period, and the columns remained anoxic throughout the experiment (Figure A.28). The DO was depleted within the top 15 cm media plus barrier sand. The columns lowered the pH of the column influent (7.43 ± 0.13) to 6.80–6.95 in the column effluent while not affecting the electrical conductivity (influent = 343 ± 23 μS cm⁻¹) or total dissolved solids (influent = 172 ± 12 mg L⁻¹). The sedimentation process also did not affect pH, electrical conductivity, or total dissolved solids (Tables A.19–A.24).

Hydraulic conductivity decreased over the course of the experiments for all the media mixtures (Table 2) but remained greater than 0.2–0.3 cm s⁻¹ for all mixtures. Biochar amendment experienced reduced column hydraulic conductivity from 0.35 ± 0.04 cm s⁻¹ to 0.21 ± 0.08 cm s⁻¹ after 62 days (32% reduction), while hydraulic conductivity loss in the RAC columns was minimal, 0.35 ± 0.04 cm s⁻¹ to 0.31 ± 0.03 cm s⁻¹ (26% reduction). The column's nominal contact time ranged from 54 to 108 min, with the zeolite and BC amendment increasing the engineered media porosity and associated contact time. The weight content measured for each mixture is reported in Table 2.

Metal Removal

Preliminary leaching tests showed the catch basin material used to create the synthetic stormwater released metals when added to water (Figure A.9). Zn (16.1 ± 4.75 μg L⁻¹) was observed in the synthetic stormwater prior to contaminant addition, indicating that dissolved Zn was loaded onto the columns during the 100 EBV conditioning period. Dissolved metal concentrations in the influent fluctuated from the target spike concentration (30 μg L⁻¹) over the course of the experiment (Table 3 and Figure A.30), likely because of sorption/desorption and complexation with suspended catch

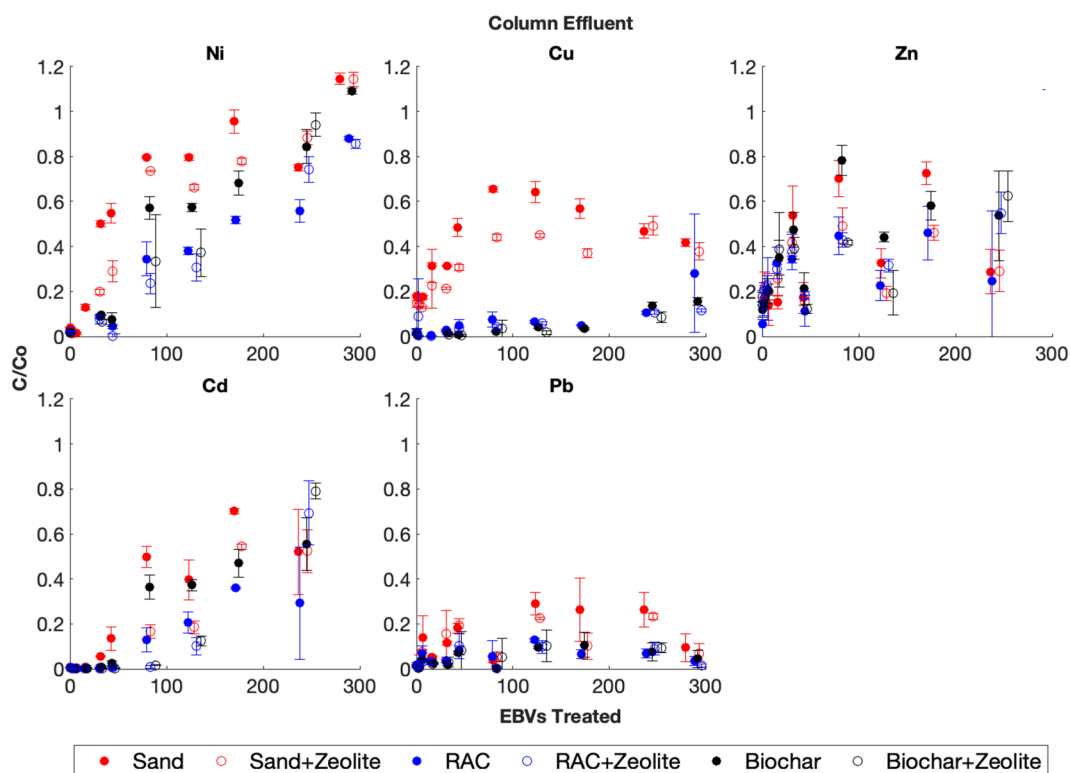


Figure 2. Dissolved metal transport and breakthrough over the first 300 empty bed volumes treated ($n = 3$).

basin material and heterogeneity in the catch basin material. Aqueous concentrations of Pb, in particular, were very low, likely because of Pb interaction with suspended catch basin material. Visual Minteq equilibrium software confirmed that in the absence of suspended solids, the metals are expected to be in dissolved forms at their target concentration in the synthetic stormwater based on the major ions present. Therefore, Pb removal can be attributed to suspended particle removal through physical filtration by the engineered media.

Dissolved metal removal occurred in all the columns to various degrees based on the engineered media mixture and metal species (Table 3 and Figure 2). The sand columns experienced initial metal removal for all the metals analyzed, which may be attributed to surface chemisorption on the surface of sand grains.³⁰ Dissolved metals removal in the sand columns (C/C_0) were in the order $Pb > Cd > Cu > Ni > Zn$ (Table 3), though note that the dissolved metal concentrations varied among the group of metals included (Table 3, Figure A.30). While Pb was largely particle-associated and thereby removed by physical filtration, low dissolved Pb concentrations were observed in the sand column effluent, indicating that small amounts of Pb can still pass through unamended sand columns.

Zeolite contributed some benefit for metal removal but less than that reported by others.^{6,30} Reddy et al. (2014) found zeolite to remove significantly more Cd, Cu, Pb, Ni, and Zn than sand in batch tests with initial concentrations ranging as high as 300 mg L^{-1} .³⁴ Charters et al. (2021) found zeolite to effectively remove Zn and Cu from roof water runoff.⁴¹ The poor performance of zeolite in this study may be attributed to the experimental conditions, including relatively low dissolved metal concentrations, relatively low contact time, the presence of DOC, and preloading of Zn during the conditioning phase.

Zeolite removal of metals is sensitive to ionic strength (particularly Na^+ , Ca^{2+} , and Mg^{2+}) and dissolved metal concentration⁴² and inhibited by dissolved components in stormwater.²⁷ Nguyen et al. (2015) found zeolite in column experiments to have a lower adsorption capacity than the same material in batch experiments, possibly because of lower metal–zeolite contact time in the column experiment.⁴³ Dissolved metals may complex with DOC and become unavailable for cation exchange on the surface of zeolite,⁴⁴ and DOC is generally adsorbed to the outer surface of zeolite, thereby preventing metal species from accessing the interior of the zeolite.⁴⁵ Finally, dissolved Zn may have already occupied many of the cation exchange and adsorption sites on the zeolite during the conditioning phase, reducing the efficacy of the zeolite during the challenge tests.

Overall, BC amendment reduced dissolved metal concentrations more than zeolite. Greater removal efficacy of BC amendment relative to zeolite aligns well with observations in previous studies.³¹ BC amendment removed metals in the order of $Pb > Cu > Cd > Ni > Zn$ as shown in Table 3 where breakthrough is defined as 40% of influent concentration as a consistent benchmark to assess transport for each studied contaminant. RAC amendment provided slightly better removal than biochar for nearly all metal species, though the difference is not substantial. Combining zeolite and BC amendment improved metal removal more than zeolite or BC alone. This is significant because the combined zeolite–BC mixture had equal or less zeolite and BC while improving performance. One explanation for this is that the BC amendment reduced the DOC in the column, thereby reducing the DOC interference with the zeolite and the potential for DOC to complex with metals.

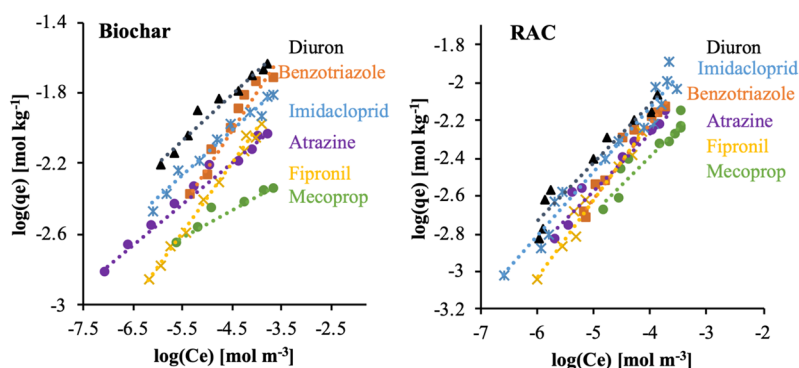


Figure 3. Batch isotherms conducted with biochar (left) and RAC (right) with the same suite of contaminants, background DOC, and water quality conditions as used in the column experiments. Contaminant concentrations in the batch tests ($100 \mu\text{g L}^{-1}$) were increased from levels used in the column experiments ($40 \mu\text{g L}^{-1}$) to facilitate analysis.

Table 4. Comparison of Empty Bed Volumes Treated for Hyphil-TrOCs as Indicated by $C/C_0 = 0.4$ at the 25% Sample Port

eng. media mix	EBV treated until $C/C_0 = 0.4$ at 25% sample port ^b											
	benzotriazole		atrazine		diuron		fipronil		imidacloprid		mecoprop	
sand	<1	±0	<1	±0	<1	±0	<1	±0	<1	±0	<1	±0
+ zeolite	<1	±0	<1	±0	<1	±0	<1	±0	<1	±0	<1	±0
+ RAC	164	±14	39	±60	260	±43	1	±1	98	±45	6	±1
+ biochar	>450	— ^c	154	±14	>450	— ^c	100	±44	>450	— ^c	39	±24
+ zeolite + biochar	>450	—	150	±16	>450	—	134	±86	>450	—	46	±10
+ zeolite + RAC	359	±56	82	±34	>450	—	17	±3	162	±8	5	±1
inf. conc. ^a [$\mu\text{g/L}$]	29.1	±3.1	42.3	±4.2	54.1	±4.5	33.0	±2.7	51.6	±4.2	50.6	±6.1

^aTime weighted average \pm standard deviation ($n = 3$). ^bMean \pm standard deviation ($n = 3$) [EBVs]. ^c— Indicates no calculated value because of lack of observed contaminants in sample.

Hydrophilic TrOC Removal

Batch isotherms conducted over 90 days with similar stormwater matrix conditions as in the column experiment are shown below in Figure 3. The same amount of DOC was added to the batch test jars, however because of the inhibition of biological growth for the isotherm measurements, the background DOC (9.7 mg C L^{-1}) was greater than observed in the column influent. The order of compound affinity to BC observed in the isotherms generally matched the observed transport in the column experiments, with fipronil and mecoprop the most mobile contaminants in the column experiments also sorbing least to the BC in the batch isotherm experiments. Biochar appears to sorb more contaminants than RAC on a per-mass basis, which is consistent with the superior initial performance of biochar in the column experiments.

While RAC surface area ($\sim 800\text{--}1100 \text{ m}^2 \text{ g}^{-1}$) is greater than biochar used in this study ($499 \text{ m}^2 \text{ g}^{-1}$) and would suggest that RAC has a greater sorption capacity than biochar, the biochar appeared to sorb more contaminants than RAC on a mass basis, as shown below in Figure 3. The reduction in sorption capacity in the BC may be due to competition and interference from the background DOC and may be more significant for RAC than biochar, as the sorption capacity of RAC is larger than biochar in the absence of DOC.⁴⁶ Koelmans et al. found that increasing humic acid loadings decreased the isotherm slopes while increasing the nonlinearity of isotherms describing PCB sorption to charcoal, indicating more competition at the surface.⁴⁷ Pignatello et al. found that humic acid and fulvic acid suppressed organic compound adsorption in proportion to increasing DOC molecular size and thus contribute to pore blocking or act as competitive

adsorbates.⁴⁶ Quinlivan et al. reported that the ratio of the size of pores to the kinetic diameter of the adsorbate was crucial to preventing pore blockage or constriction due to DOC adsorption and that micropollutant adsorption capacity decreased more dramatically in adsorbents with smaller pores.⁴⁸ Thus, the larger pore sizes in biochar used in this work compared to RAC (Figures A.18 and A.19) may contribute to the reduced inhibition of contaminant removal capacity caused by DOC. Ongoing efforts are evaluating the equilibrium sorption partitioning for dynamic modeling of contaminant transport in the column system.

Dissolved influent concentrations of hyphil-TrOCs in the column test were $29\text{--}54 \mu\text{g L}^{-1}$ and remained in this range throughout the experiment (Table 4 and Figure A.35). Variation between targeted spike concentration ($40 \mu\text{g L}^{-1}$) and observed concentration is likely due to interaction with suspended catch basin material, which appeared to reduce the dissolved concentration of benzotriazole and fipronil most significantly. Data in Figure 4 show that BC-amended columns removed nearly all of the hyphil-TrOCs over the course of the experiment, while the sand columns and zeolite alone saw no appreciable reduction in hyphil-TrOCs. When combined with BC, zeolite gave a slight improvement in performance, even though the zeolite-BC columns have equal or less mass of BC. This is likely due to the slight increase in contact time resulting from the increased porosity of the zeolite relative to sand (Table 2). Hyphil-TrOCs were removed to a much greater extent than metals.

Measurements at the 25% and 50% sample ports (Figures 4 and A.36) provide a view of hyphil-TrOCs migration within the column. For example, samples from the 25% sample port show that biochar reduced hyphil-TrOCs transport more than

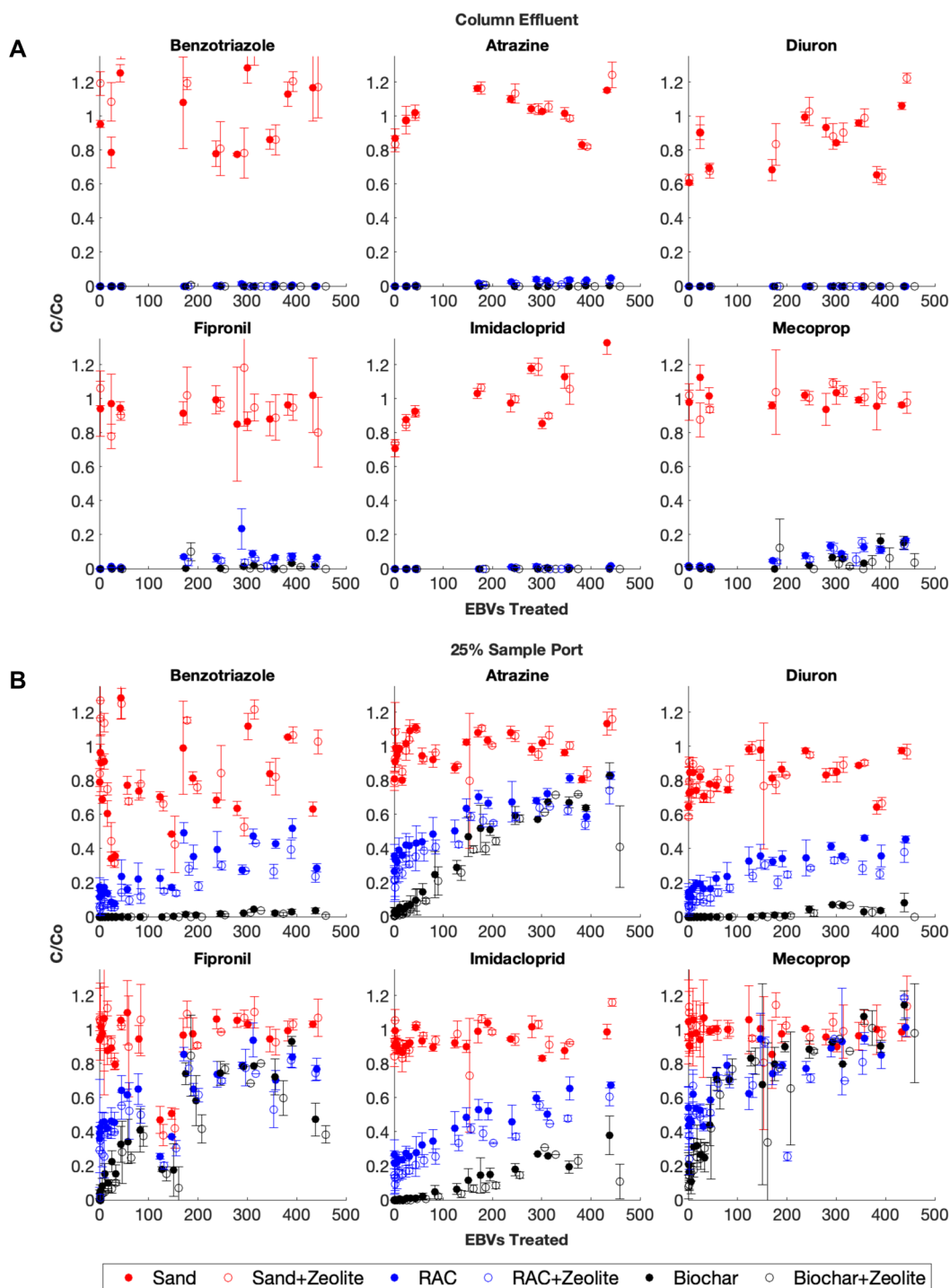


Figure 4. Dissolved hydrophilic TrOCs transport and breakthrough in the column effluent (A) and 25% sample port (B) (depth = 15 cm media). Error bars indicate one standard deviation above and below the mean ($n = 3$).

RAC. This improved benefit of biochar amendment relative to RAC is notable since there is greater mass of RAC in the column (153 g) than biochar (90 g, Table 2). However, the observed performance difference between RAC and biochar may be due to RAC's sorption kinetics and differences in porosities resulting in shorter contact time (67 min for RAC, 92 min for biochar; Table 2) and the influence of background DOC. The rapid initial breakthrough observed at the 25% and 50% sample ports in the RAC columns indicates that sorption is kinetically limited, and the kinetics favor contaminant

removal in the biochar-amended columns. Biochar has a substantially lower density (0.103 g mL^{-1}) than that of RAC (0.559 g mL^{-1}), so although the mass of biochar is less than RAC, the volume of biochar is substantially greater (30 vol %) than that of RAC (10 vol %).

This difference in density and volume may be a function of the pore size distribution and plays an important role in biochar's faster kinetics. Biochar's larger pores may facilitate faster contaminant transport into the interior of the carbon grains than RAC (Figures A.18 and A.19), especially in the

Table 5. Comparison of Empty Bed Volumes Treated for PFASs as Indicated by $C/C_0 = 0.4$ at the 50% Sample Port

eng. media Mix	EBV treated until $C/C_0 = 0.4$ at 50% sample port ^{b,c}											
	PFHxA		PFOA		PFHxS		PFOS		Cl-PFOS		FHxSA	
sand	<1	±0	<1	±0	<1	±0	<1	±0	<1	±0	<1	±0
+ zeolite	<1	±0	<1	±0	<1	±0	<1	±0	<1	±0	<1	±0
+ RAC	3	±2	45	±49	53	±61	75	±36	92	±52	1	±0
+ biochar	13	±1	76	±38	79	±27	93	±43	114	±25	69	±15
+ zeolite + biochar	38	±35	115	±27	122	±4	157	±26	202	±16	102	±20
+ zeolite + RAC	8	±10	157	±109	80	±55	199	±63	111	±74	16	±24
inf. conc. ^a [ug/L]	74.3	±14.9	98.1	±17.9	440	±68	2900	±600	47.3	±17.6	69.4	±30.1

^aTime weighted average ± standard deviation ($n = 3$). ^bMean ± standard deviation ($n = 3$) [EBVs]. ^cPFHxA is perfluorohexanoic acid; PFOA is perfluorooctanoic acid; PFHxS is perfluorohexanesulfonate; PFOS is perfluorooctanesulfonate; Cl-PFOS is chloro-perfluorooctanesulfonate; FHxSA is perfluorohexane sulfonamide.

presence of DOC. DOC is known to generally inhibit the sorption of TrOCs on BC by reducing the effective surface area and competing for sorption sites, and reducing effective pore volume by pore-blocking.²⁵

The column experiments with biochar or RAC employed low weight percent sorbents (Table 2) in order to observe transport of TrOCs. The relative transport of the hyphil-TrOCs is in the order mecoprop > fipronil > atrazine > imidacloprid > benzotriazole > diuron. Interestingly, this order does not correlate with solute K_{ow} or solubility but instead agrees with the measured equilibrium isotherm sorption capacity. Relative transport may be impacted by background DOC and compound-specific properties such as molar volume, polar surface area, and charge. The order of compound mobility appears to be consistent between biochar and RAC, though the difference in performance between biochar and RAC appears to decrease as the compound mobility increases, with mecoprop having the smallest difference in performance. At a pH of 6.80–6.95, mecoprop exists as an anionic species and therefore experiences electrostatic repulsion from the negatively charged BC surfaces and inhibits its ability to diffuse into BC's pores because of their negatively charged surface.²⁶ Dechene et al. observed that biochar amendment of soil did not show any benefit for three anionic polar herbicides, perhaps because of electrostatic repulsion, while there was significant benefit for a neutrally charged polar herbicide.⁴⁹

PFASs Removal

Dissolved influent concentrations of PFOS were 2900 ± 600 ng L⁻¹ throughout the experiment (Table 5 and Figure A.40). Influent and sand column concentration variability may have been impacted by variable accumulation at air–water interfaces within the experimental design (i.e., the constant head overflow return; Figure 1). The six PFASs measured and reported here (PFHxA, PFOA, PFHxS, PFOS, Cl-PFOS, and FHxSA) were best removed with BC amendment and negligibly removed in the sand and sand–zeolite columns (Figure 5 and Table 5). While biochar appeared to have better or equivalent removal performance initially, RAC performed better over the course of the experiment. Similarly to the hyphil-TrOCs, zeolite addition to the BC-amended mixtures improved PFASs removal, likely because of the increased contact time resulting from zeolite's increased porosity relative to sand.

Of the PFASs with six perfluoroalkyl carbons (i.e., C6), PFASs species mobility is ranked PFHxA > FHxSA > PFHxS, as observed in Table 5. PFASs with eight perfluoroalkyl carbons (i.e., C8) ranked similarly with respect to species

mobility: PFOA > PFOS > Cl-PFOS; steric effects and electronegativity differences between hydrophilic functional groups likely contribute to the differences in mobility across both carbon lengths. Long-chain C8 PFASs were better removed than shorter-chain C6 PFASs, as shown in Table 5 for both the RAC and biochar columns. This is fully expected because of steric effects on hydrophobic interactions and surface aggregation and has been widely observed in the literature.^{50,51} Furthermore, stormwater is a complex medium for PFASs sorption, as sorption may be hindered by the presence of DOC in stormwater⁵² but increased via electrostatic interactions by the presence of divalent cations such as calcium that are commonly found in stormwater.^{53,54}

Effluent concentrations were observed to exceed influent values in some cases. An increase in semistable intermediates such as FHxSA can be expected because of transformation of precursors present in the AFFF spike solution such as AmPr-FHxSA, as illustrated by recent experimental evidence in soil columns,^{55,56} although investigation of such transformation is beyond this study's scope. Some observed effluent concentrations relative to influent concentrations are likely high as a result of variability in influent concentration variation. PFOS, the best removed of the studied PFASs, has similar performance to mecoprop, the least removed of the studied hyphil-TrOCs.

PRACTICAL IMPLICATIONS

This study shows that the studied BC amendment—whether high-temperature gasification biochar or RAC—effectively removes a suite of metals, hydrophilic TrOCs, and PFASs from stormwater runoff while maintaining sufficient hydraulic conductivity. While zeolite provided slight benefits for metals, hyphil-TrOCs, and PFASs removal under the studied conditions, the benefit was not substantial and likely was due to the increased porosity and detention time of the zeolite relative to the sand. RAC amendment provided greater benefit for PFAS removal than biochar. Biochar amendment appeared to be more effective for hyphil-TrOC removal even though there was more RAC present on a wt % basis. While biochar ($\$262 \text{ m}^{-3}$) costs less than RAC ($\763 m^{-3}) and virgin AC ($\$1630 \text{ m}^{-3}$) on a volume-basis, biochar costs more ($\$2.53 \text{ kg}^{-1}$) than RAC ($\1.5 kg^{-1}) on a mass-basis because of the significant difference in material density (Table 6). This raises questions about which material may be more beneficial for widescale use in SCMs where cost is an important consideration and SCMs are built to specific material-standards rather than based on individual site conditions.

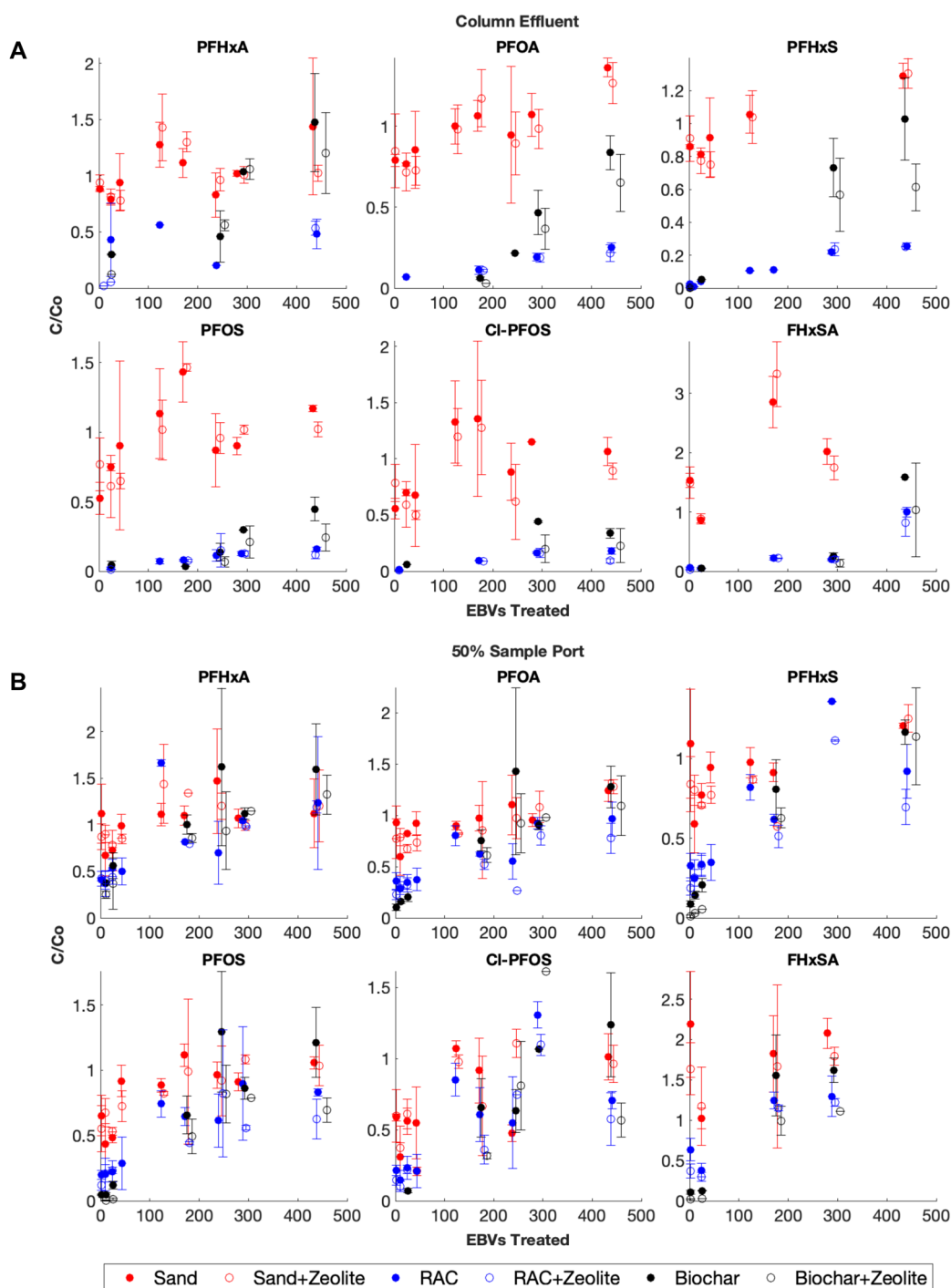


Figure 5. Dissolved PFAS transport and breakthrough in the column effluent (A) and 50% sample port (B). Error bars indicate one standard deviation above and below the mean ($n = 3$).

Table 6. Cost Estimates for BC Amendment Used in This Study

parameter		biochar ^a	RAC ^b	AC ^c
cost by mass	\$ kg ⁻¹	2.54	1.50	3.19
density	kg m ⁻³	103	510	510
cost by volume	\$ m ⁻³	262	763	1630

^aBiochar Supreme Environmental Ultra, WA. ^bNorit GAC 830R.

^cCalgon AC.

For example, constructing a filter with RAC will likely be less expensive than biochar if designs call for a certain wt % BC content, while the opposite is likely true if designs call for a specific vol % BC content. In terms of performance, using a set volumetric content will likely yield better performance for a RAC system while using a set mass content will yield better performance for a biochar system. Further, because of the clogging concerns due to increased friability and reduction in hydraulic conductivity associated with biochar relative to RAC, constructed systems may not be able to contain as much biochar (on either a wt % and vol % basis) as RAC, likely

limiting their maximum potential treatment life. These experiments with biochar and RAC employed low weight percent to observe transport of TrOCs and a design consideration is an optimal weight percent for longer performance and sustained hydraulic conductivity. A full life cycle assessment including handling, maintenance, and material sustainability considerations is needed to determine individual selections of biochar or RAC for general SCM guidance. Because of the nonuniformity of biochar material, production methods, cost, and performance (especially relative to RAC), individual life cycle assessments must include specific biochars. This work found that the studied biochar and RAC are both capable of effectively removing a broad suite of dissolved co-contaminants under relatively high-flow conditions with representative grain sizes and synthetic stormwater and are worthy of further study.

This study identified an important trade-off between contaminant removal performance and flow rate. Previous studies have shown successful contaminant removal at slower flow rates and with smaller-sized media particles for which filter lifetime is a function primarily of sorption capacity.¹⁶ This study shows that successful contaminant removal is possible at higher flow rates in which filters must be designed with larger sized media and for which sorption kinetics become an important factor. Increasing the treatment flow rate of stormwater control measures reduces the amount of stormwater that must be detained for a controlled flow and therefore reduces the total footprint of the system. Reducing the footprint is especially important in urban areas and at industrial facilities where space is often limiting. More work is needed to fully understand the impact of flow rates on design and validate a contaminant transport model at higher flow rates. Still, this study shows that adequate contaminant removal is possible at flow rates of 20 cm hr⁻¹.

Maintenance is an important performance consideration for BC-amended stormwater control measures. Too often, maintenance is overlooked and stormwater control measures clog or are overgrown. In this study, the downflow configuration with continued TSS loading was chosen to better replicate field-operation conditions in which clogging would be a concern. The barrier sand at the top of the filter in this study was designed to trap particles and was vacuumed and replaced every 6–8 days to remove biologic growth and trapped suspended particles. Maintaining the top layer of barrier sand helped ensure that the filters operated at their design flow. While plants have been shown to provide a benefit to maintaining adequate hydraulic conductivity,⁵⁷ some locations may not be able to be planted because of space or wildlife concerns. In these instances, maintaining a layer of barrier sand at the top of the filter may provide an easy method for maintaining the hydraulic conductivity of the filter and preventing the filter from clogging.

CONCLUSIONS

Engineered filters with BC amendment are a promising technology for the treatment of stormwater runoff. Filters operated in a gravity-driven down-flow mode were conditioned for 100 EBVs and then challenge tested for 480 EBVs with a wide suite of co-contaminants at elevated concentrations, including metals, hydrophilic and hydrophobic TrOCs, and PFASs. Filters were operated with consistent TSS and DOC loading without clogging with periodic maintenance during which the top layer of barrier sand was cleaned and replaced.

Filters amended with high-temperature gasification biochar or regenerated activated carbon removed a suite of metals, TrOCs, and PFASs while removing nearly all TSS and reducing turbidity. Zeolite did not appear to substantially benefit the contaminant removal in this study. Contaminant transport in the columns indicate that the TrOC removal is kinetically limited at face velocity flow rates at 20 cm/h. This study offers proof-of-concept for BC-amended engineered media filters as effective stormwater control measures. While this study used relatively high concentrations of contaminants and low BC contents in order to observe contaminant transport, performance in the field is likely to be significantly better with higher BC-content filters and lower ambient stormwater contaminant concentrations. Additional modeling, using the contaminant transport observed in this study, may be used to estimate field performance and understand the design implications of kinetically limited contaminant removal performance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenvironau.2c00037>.

Detailed information on the experimental design, including all the chemicals used, analytical parameters, column experimental system, water quality, and contaminant results (PDF)

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Notes

The authors declare no competing financial interest.

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