

Research Paper

Treatment of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in stormwater using polishing columns with biochar and granular activated carbon

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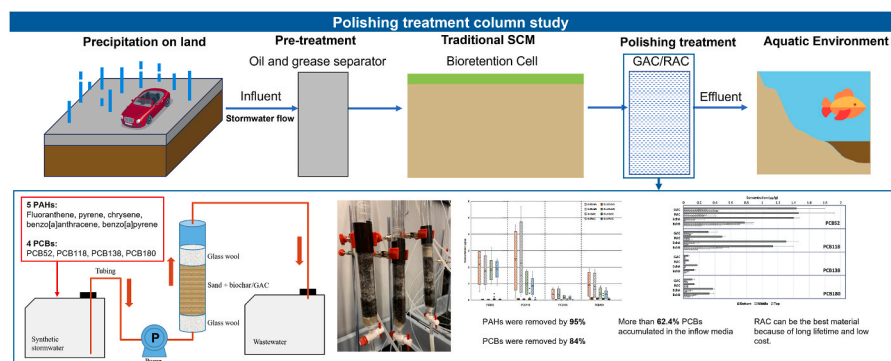
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HIGHLIGHTS

- Outflow from stormwater bioretention cells contain dissolved PAHs and PCBs despite treatment.
- Biochar and granular activated carbon were tested to remove dissolved PAHs and PCBs from bioretention outflow.
- 95% and 84% of PAHs and PCBs were removed, respectively.
- Treatment efficiency of PAHs and PCBs was influenced by the molecular structure and size of the contaminants.

GRAPHICAL ABSTRACT



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ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) are recalcitrant organic pollutants often detected in stormwater. Various stormwater control measures (SCMs) can remove PAHs and PCBs by filtration, adsorption, and biodegradation. However, dissolved PAHs and PCBs remain present in the treated outflow of SCMs. To provide further treatment, two types of biochar (biochar A and biochar B), a granular activated carbon (GAC), and a regenerated GAC (RAC) were tested in a column study with synthetic stormwater containing PAHs and PCBs in low concentrations. Results showed that PAH concentrations were reduced by 98.2–99.8% (range: <limit of quantification (LOQ) - 1.89 µg/L), while PCB concentrations were reduced by 86.0–97.9% (range: <LOQ - 0.7 µg/L). The extraction of PCBs from the media showed that >62% of the PCBs accumulated at the first third of the column due to adsorption onto the black carbon material thus providing information for management. The difference in treatment performances of different PAHs and PCBs may be caused by the molecular structure of the contaminants. Lifetime calculations indicated that biochar had lifetimes >36–51 years, while GAC and RAC showed lifetimes longer than 147 and 206 years, respectively, based on predicted precipitation for scaled up designs. The results showed that biochar and activated carbons can be efficient adsorbents for stormwater polishing treatment. With consideration of efficiency, sustainability and cost, RAC is recommended for polishing treatment of dissolved PAHs and PCBs.

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1. Introduction

Urban stormwater is a major source of natural water impairments, with implicated pollutants that include heavy metals, persistent organic pollutants, pesticides, nutrients and pathogens (Gasperi et al., 2012; Ivanovsky et al., 2018; Masoner et al., 2019). Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are two groups of organic pollutants that are frequently detected in urban stormwater, where they can pose a risk due to their toxicity, where some congeners are carcinogenic, teratogenic, and/or mutagenic. Due to their hydrophobicity (high Kow), PAHs and PCBs will bioaccumulate in the environment (Ololade et al., 2021). Consequently, if untreated stormwater containing PAHs and PCBs is discharged into aquatic environments, it will not only impact aquatic life but also increase potential threats to human health (Nakata et al., 2003). It is necessary to remove PAHs and PCBs from stormwater before discharge to reduce this environmental concern.

Stormwater control measures (SCMs), such as green roofs, biofilters, permeable pavement, and vegetated swales, are being used for flood control and contaminant reduction from stormwater runoff (Wolfand et al., 2019). Filtration-based SCMs can effectively remove particulate matter (total suspended solids, TSS) by sedimentation and filtration, and thus remove pollutants absorbed on these particles (Landsman and Davis, 2018). Bioretention cells are stormwater SCMs which are used worldwide for stormwater treatment (Flanagan et al., 2019; Lucas and Greenway, 2011; Shafique, 2016), removing pollutants by a combination of natural and engineered processes employing a soil-based bioretention media mix. As a result, processes such as biodegradation, phytodegradation, adsorption, and filtration can be carried out within the bioretention cells (LeFevre et al., 2015; Muerdter et al., 2018). However, dissolved pollutants can still pass through SCMs and be discharged into the environment (LeFevre et al., 2015). Previous studies in various places and under different environmental conditions have observed that PAHs and PCBs cannot be completely removed by bioretention treatment (Biswal et al., 2022; Cao et al., 2023; David et al., 2015; DiBlasi et al., 2008; Flanagan et al., 2019, 2021; Gilbreath et al., 2019).

To meet stringent discharge requirements for these recalcitrant organic pollutants and further remove dissolved PCBs and PAHs in the effluent, implementation of a polishing treatment process would be an added complement to conventional stormwater control measures. Biochar and Granular Activated Carbon (GAC) are two types of adsorbent materials commonly used in water treatment to remove contaminants such as heavy metals, pharmaceuticals and personal care products, other organic compounds, and nutrients (Castiglioni et al., 2022; Huggins et al., 2016; Palansooriya et al., 2020). Biochar and GACs have been previously used to treat PAHs in water (Lamichhane et al., 2016) and treatment of PCBs in soil and sediments has been carried out using biochar and GAC (Denyes et al., 2013; Hilber and Bucheli, 2010). The treatment capacity of exhausted GAC can be recovered by regeneration and then reused for water treatment (Larasati et al., 2021). As a result, biochar, GAC and regenerated GAC (RAC) are promising materials for polishing treatment of stormwater.

The objectives of this study were as follows: (1) to evaluate the potential of utilizing biochar, GAC, and/or RAC as a polishing treatment media for the removal of PAHs and PCBs from stormwater, (2) to evaluate breakthrough of different polishing media under conditions of low/moderate dissolved PAH and PCB concentrations, and (3) to compare performance of biochar and GAC as polishing treatment media. To achieve the objectives, synthetic stormwater with selected dissolved PAHs and PCBs (to simulate stormwater that has been treated through a conventional SCM, with all particulates being removed) was pumped through columns containing biochar, GAC, and RAC, and PAH and PCB removals were quantified. Removal curves were found for the pollutants, and media lifetime are estimated based on the breakthrough time.

2. Materials and methods

2.1. Column setup

A model system with polishing treatment columns and synthetic stormwater was set up to evaluate removal and breakthrough of PAHs and PCBs. This study used columns filled with selected black carbon materials: two different types of biochar, a GAC, and a RAC. Both biochar materials had pine wood feedstock. The pyrolysis temperature of the biochar was selected based on the target stormwater pollutants (metals, PAHs, PCBs). High pyrolysis temperature increases adsorption of organics, while reducing adsorption of metals (Hassan et al., 2020); pyrolysis temperature >500 °C improves the longevity of biochar (Ippolito et al., 2020; Kaya et al., 2022). The pyrolysis temperature of biochar A (BchA) (Biochar Solutions, Lafayette, U.S.) was 550 °C, and that of biochar B (BchB) (Biochar Now, Loveland, U.S.) was 550–600 °C. Filtrasorb® F400 (Calgon Carbon, Pittsburgh, U.S.) was the GAC and Calgon Carbon® DSR-C (Calgon Carbon, Pittsburgh, U.S.) was the RAC in this study (Table 1).

Fig. 1 shows a schematic of the column setup. The column study was conducted using glass columns with 2.4 cm internal diameter. Twelve columns in total, with three replicate columns for each selected material set up during two experimental rounds. To promote a rapid breakthrough, 6 g of each biochar, GAC, and RAC were mixed with 127 g of 20–30 silica sand (Certified Material Testing Products, Palm Bay, U.S.) and packed into the columns to a bed height of approximately 20 cm. About 3 cm of glass wool (Acros Organics, Geel, Belgium) was placed at the bottom and the top of the column for even distribution of the synthetic stormwater through the column, which helped prevent loss of the geomedia. The short section of tubing used for pumping was made of FKM (Fluorocarbon) (Masterflex, Gelsenkirchen, Germany) and other tubing in this study was made of PTFE (Polytetrafluoroethylene) (Cole-Parmer, Vernon Hills, U.S.); the reservoirs used were HDPE (High-density polyethylene) (Priority Plastics Inc, Portland, U.S.). After completion of the column study, the media was poured from the top of the column and divided into thirds based on mass and collected for further analysis.

The particle size of the black carbon materials used in this study was <2 mm, and the sand had a particle size range of 0.84 to 0.60 mm. The average particle size of the polishing media ranged from 0.89 to 0.66 mm, and as a result, the ratio of column diameter and particle size ranged from 40 to 27, suggesting that wall effects can be neglected (Chu and Ng, 1989).

2.2. Synthetic stormwater recipe

According to the previous study, due to the time and location, pollutants in urban stormwater can exhibit a large variation in concentration. The highest fluoranthene concentration (36700 ng/L) has been recorded as 3336 times of the lowest concentration (11 ng/L) (Masoner

Table 1
Material characteristics for Biochar, GAC, and RAC adsorbents.

Vendor	Column	Surface Area (m ² /g)	bulk density (g/cm ³)	Micropore volume (cm ³ /g)
Biochar Solutions	BchA	237	0.09	NA
Biochar Now	BchB	400	NA	NA
Calgon Carbon, F400	GAC	1050	0.54	^a 0.296
Calgon Carbon, DSR-C	RAC	^a 723	0.6	^a 0.367

^a Data source: Zhang et al. (2005), other data were provided by vendors. NA: data not available.

et al., 2019). The total PCB concentration can range from 0.18 ng/L to 727 ng/L – a difference of 4038 times (Pamuru et al., 2022). As a result, in order to conduct continuous column experiments, to ensure the influent concentrations were quantifiable, and to make the experiments more controllable, synthetic stormwater was used in this study.

A synthetic stormwater recipe was developed for this project (Table 2) and used dechlorinated tap water. The selected PAHs and PCBs congeners were chosen based on a range of molecular weights, toxicity, and observations from other stormwater studies (Zgheib et al., 2012). Studies show that the major PAHs in stormwater were medium-molecular weight PAHs (MMW-PAHs) and high-molecular weight PAHs (HMW-PAHs) (Hou et al., 2020). Fluoranthene and pyrene are MMW-PAHs, while benzo[a]anthracene, chrysene, and benzo[a]pyrene are HMW-PAHs. Fluoranthene (0.090–0.025 µg/L), pyrene (0.058–0.014 µg/L), and chrysene (0.030–0.005 µg/L) are commonly detected in stormwater (DiBlasi et al., 2008). Benzo[a]anthracene and benzo[a]pyrene were included because of their high carcinogenicity (Bukowska et al., 2022; IARC, 2012).

Seven PCBs (congeners 28, 52, 101, 118, 138, 153, 180) are often detected and used as indicator PCBs (Zhao et al., 2010); of these 7 PCBs, PCB52 (12% of total PCBs in stormwater), PCB118 (8%), PCB138 (14%), and PCB180 (6%) have been detected in high levels in stormwater (Rossi et al., 2004). The four PCBs used in this research and the PCB congener groups that they represent are shown in Table S1. PAHs and PCBs used in this study were purchased from AccuStandard, New Haven, U.S.

Because of the low solubility, PAHs and PCBs were first dissolved in acetone (HPLC grade, Fisher, Pittsburgh, U.S.), then the acetone/contaminant solution was added to the synthetic stormwater reservoir. A glass bar was used for stirring of the synthetic stormwater for 5 min. Synthetic stormwater was freshly prepared every other day.

For biochar columns, acetone/contaminant solution added an additional 16 mg/L total organic carbon (TOC) to the synthetic stormwater; this value was adjusted for the activated carbon (AC) columns (1 mg/L of additional TOC was added). The concentrations of PAHs and PCBs were chosen based on 1) solubility, 2) observed concentrations in prior stormwater studies, 3) method detection limit of the protocol, and 4) a goal of achieving breakthrough at $\leq 10\%$ of influent concentration. More information on the specific PAHs and PCBs used in this study is shown in Table S2. The added PAH concentrations were in the range of detected concentrations of PAHs in stormwater, while the added PCB concentrations were higher than what has been detected in stormwater, to reach the breakthrough during the experiment and to ensure that removals could be reliably quantified.

In an attempt to mimic the characteristics of real stormwater, a leaf-based compost was used as the source of organic carbon, nitrogen, and

Table 2

Synthetic stormwater recipe for treatment train column study.

	Component	Added As	Target Concentration
Stormwater Parameters	DOC	Compost Leachate	10 mg/L
	Total nitrogen		4 mg/L
	Total phosphorus		0.25 mg/L
	Hardness (mg/L as Ca)	^a	15 mg/L
	Total dissolved solids	^a	100 mg/L
	Chlorine Suppression	NaHSO ₃	2.2 mg/L
Metals	Cu	^a	50 µg/L
	Zn	ZnCl ₂	0.2 mg/L
Organics	PAHs	Dry solid stock dissolved in acetone	
	Fluoranthene		20 µg/L
	Pyrene		20 µg/L
	Benzo[a]pyrene		1.6 µg/L
	Benz[a]anthracene		9.4 µg/L
	Chrysene		2 µg/L
	PCBs	Dry solid stock dissolved in acetone	
	52		15 µg/L
	118		13.4 µg/L
	138		1.5 µg/L
	180		3.9 µg/L

^a Means tap water already have enough this component, do not need addition.

phosphorus. Compost leachate was made using Leafgro® compost (Maryland Environmental Service, Millersville, U.S.), which was mixed with water, filtered and added as stock to achieve a final concentration of about 10 mg/L of TOC (Pamuru et al., 2022). Compost leachate stock solution was made every other day to avoid biodegradation.

Synthetic stormwater was pumped up-flow through the bottom of the columns at a constant flow rate of 1.5 mL/min (20 cm/h) by means of a peristaltic Masterflex® pump (Masterflex, Gelsenkirchen, Germany). Masterflex® L/S Platinum-Cured Silicone Tubing (Cole-Parmer, Vernon Hills, U.S.) were used for the inflow and outflow of the columns. The flow rate was selected based on the storm durations from 1 to 24 h with a 2-yr return period storm for the U.S. states of Washington (0.3–3.8 cm/h) and Maryland (0.23–1.1 cm/h), as described by Kaya et al. (2022). An intensity of 1 cm/h was selected as the upper end for Maryland and lower end of Washington and it was assumed that drainage area to treatment media area ratio was 20:1. Synthetic stormwater in the reservoirs and column effluent samples were collected in 20 mL amber bottles. Samples were analyzed for influent and effluent PAH and PCB concentrations.

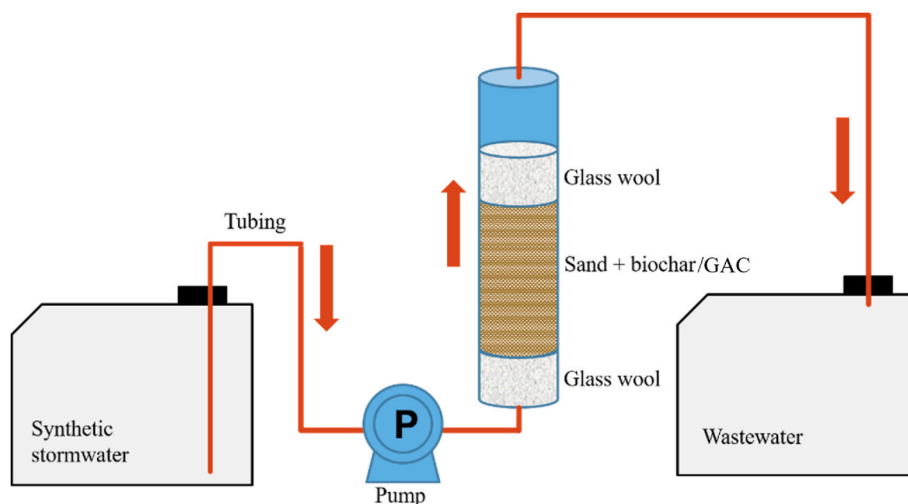


Fig. 1. Schematic of the experimental set up for the polishing treatment.

2.3. Extraction of PAHs and PCBs from water and media samples

Hexane (Fisher, Pittsburgh, U.S) and acetone (Fisher, Pittsburgh, U.S) used for extraction were HPLC grade. Surrogate standards were added into samples before extraction. Ten μL (100 mg/L) of deuterated chrysene-d12 and perylene-d12 (AccuStandard, New Haven, U.S.) were used for PAHs; PCBs surrogates were 20 μL (0.5 $\mu\text{g/mL}$) of 2,4,6-trichlorobiphenyl (PCB30) and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB204) (AccuStandard, New Haven, U.S.). Internal standards were added before samples were run on GC/MS and GC/ECD. A 10 μL mixture (100 mg/L) of Anthracene-d10 and Benzo(a)pyrene-d12 (VWR, Radnor, U.S.) was used for internal standards for PAHs, and 20 μL of the mixed solution (50 ng/mL) of Tetrachloro-m-xylene (TCMX) (VWR, Radnor, U.S.) and 2,2',4,5,5'-pentabromobiphenyl (AccuStandard, New Haven, U.S.) were used as internal standards for PCBs.

Water samples were subjected to liquid-liquid extraction to extract PAHs and PCBs. 20 mL samples were transferred into 60 mL amber vials (Restek, Bellefonte, U.S.). After addition of surrogates, 5 mL hexane was added into a 60 mL amber vial, and the vial was shaken by rotary mixer (ATR, Laurel, U.S.) for 10 min. After shaking, the liquid was left to separate for 10 min at room temperature. The hexane phase was subsequently transferred to a 60 mL glass centrifuge tube (Corning, New York, U.S.). The extraction process was repeated two more times for each sample. The hexane in the centrifuge tube was concentrated to <1 mL by a N-EVAP Nitrogen Evaporator (Organomation, Berlin, U.S.) and the concentrated samples were spiked with internal standards. Finally, hexane was added to the samples to adjust the volume to 1 mL.

To extract PAHs and PCBs from spent adsorption media, 5 g media samples were added into PTFE extraction vessels (100 mL, CEM, Matthews, U.S.) for microwave-assisted extraction (MAE) (MARS 6, CEM, City, U.S.). After the addition of surrogates, 30 mL of hexane-acetone (1:1 v/v) was added. MAE was performed at 115 °C for 10 min at 1000 W (Yuan et al., 2023). After extraction, the vessels cooled to room temperature and the solution was transferred into 60 mL amber vials. Residues were rinsed using 5 mL of hexane, hexane-acetone (1:1), and acetone separately, and the supernatants were transferred to amber vials. Then, the extracts were concentrated to 1 mL by nitrogen flow. Clean sea sand (Merck, U.S.) was used as a blank. After extraction, the extracts were cleaned by an alumina column; the extract was loaded on the column and eluted with 20 mL hexane-dichloromethane (3:2) (v/v). The column effluent was collected in a graduated centrifuge tube; the sample was then concentrated to less than 1 mL by nitrogen flow. The cleaned extracts were spiked with internal standards, and hexane was added to produce a final volume of exactly 1 mL.

2.4. Chemical analysis

Samples were analyzed by gas chromatography/mass spectrometry (GC/MS) (7890B, Agilent Technologies, Santa Clara, U.S.) for PAHs with an Agilent fused silica capillary column (HP-5ms) and a mass spectrometer detector (5973 N, Agilent Technologies, U.S.) operated in the selected ion monitoring (SIM) and Scan mode. PCB analysis used gas chromatography/Electron Capture Detector (GC/ECD) (7890B, Agilent Technologies, U.S.) with an Agilent fused silica capillary column (HP-5ms). The carrier gas was helium, and the injection was in splitless mode with a volume of 1 μL . The temperature of the oven was raised from 70 °C to 180 °C at 7 °C min⁻¹, from 180 °C to 225 °C at 1 °C min⁻¹, from 225 °C to 285 °C at 5.8 °C min⁻¹ with isothermal hold at 285 °C for 20 min, then ramped to 300 °C at 11.5 °C min⁻¹ and held at 300 °C for 10 min. TOC analyzer (TOC-L, Shimadzu, Japan) was used to analyze TOC in water samples. 1–100 mg/L glycine standard solution was used to make the calibration curve.

2.5. Quality control and quality assurance

To avoid contamination of water and media samples, all containers

were made of glass or PTFE. The glassware was cleaned by hexane, methanol (Fisher, Pittsburgh, U.S), and DI water, and baked at 550 °C for 4 h before experiments. To avoid contamination between extractions, PTFE extraction vessels were ultrasonicated with hexane and methanol and then rinsed with DI water after sonication. To avoid contamination in the GC-MS column, a hexane injection was added at the first and last of the run sequences.

The recoveries for PAHs and PCBs were determined by surrogate standards, with acceptable range for recoveries selected as 50–125% (Hermanson and Johnson, 2007). To avoid possible bias caused by the recovery of different compounds, all data of the sample that had any one surrogate recovery outside the range were not included in the data analysis. PAHs extracted from water samples had recoveries from 5.9% to 139.3%, and data from 3 samples were removed (BchB1 at 48 bed volumes, GAC3 at 96 and 263 bed volumes). All PAHs extracted from media had surrogate recoveries <50%; as a result, PAH accumulation in polishing media is not presented. PCBs from water samples had recoveries from 20.9% to 124.7%, and data from 2 samples were removed (BchB2 at 48 bed volumes, and RAC1 at 886 bed volumes). PCBs from polishing media samples had recoveries from 32.7% to 99.4%, and data from 1 sample was removed (GAC3 middle media). The instrument detection limit (IDL) was set as the lower end of calibration curve, with 7 measurements compared with 20 blanks using a *t*-test; the detailed processes are presented in the Supplementary Material. Method detection limit (MDL) was calculated by the following processes: PAH and PCB standards were spiked into 40 mL DI water and extracted as the same method mentioned above. Seven spiked samples were extracted and the detailed processes are shown in the Supplementary Material. Limit of quantification (LOQ) was set as the larger value of IDL and MDL. The values of LOQ are shown in Table S3. For compounds that have some concentrations lower than the LOQ, concentrations below LOQ are represented as LOQ/2 for removal calculation and plots; concentrations below LOQ were reported as < LOQ and not used for other calculations. For compounds that have all concentrations in outflow samples lower than the LOQ, the compounds were removed from analysis.

2.6. Data analysis

Effluent to influent concentration ratios (C/C_0) were calculated for all column samples, and to evaluate the treatment efficiency. Samples from each adsorbent were completed in duplicate. The individual concentrations for PAH and PCB congeners of influent and effluent samples and C/C_0 value of different columns were compared by one-way ANOVA test, and post-hoc analysis by Tukey's method was applied for comparisons among columns; statistical significance of all tests was set at $p = 0.05$.

3. Results and discussion

3.1. Overall treatment capacity of columns

For the biochar columns, PAHs and PCBs were measured until 383 bed volumes of synthetic stormwater were pumped through the columns. Because no breakthrough was observed, more stormwater (886 bed volumes) was pumped through GAC and RAC columns and still exhaustion was never noted in the columns. Although the amounts of PCBs and PAHs added to synthetic stormwater was not purposely changed, the measured concentrations of inflow PAHs and PCBs varied greatly. All outflow benzo[a]pyrene concentrations were below LOQ; as a result, quantification of benzo[a]pyrene is not available.

Biochar columns and AC columns had inflow TOC concentrations in the range of 8.5–65 mg/L and 9.6–13.5 mg/L, respectively. The biochar columns showed higher TOC concentration than AC columns because more acetone was added in synthetic stormwater to dissolve the organic pollutants (PAHs, PCBs). Biochar columns showed outflow concentrations of TOC that were higher than the inflow concentration, which was

25 ± 16 mg/L. After the treatment with AC columns, the TOC concentration was reduced by 20% to 8.6 ± 0.68 mg/L. The increase of TOC in the biochar columns may be caused by leaching of TOC from the biochar and the transport of biochar colloids, which may not be removed effectively during the dry sieving. Due to the lower production temperatures, biochar contains organic carbon that is less recalcitrant than ACs, which may cause DOC leaching from the media (Huang et al., 2019).

3.2. Concentrations of PAHs and PCBs

Inflow and outflow concentration of PAHs were analyzed and fluoranthene demonstrated the highest inflow concentration variation (Fig. 2), which ranged from 1.7 $\mu\text{g/L}$ to 184 $\mu\text{g/L}$. Since the TOC of the synthetic stormwater was contributed by adding compost leachate, it is possible that small particulate matter in the compost leachate caused the uneven distribution of organics. Nonetheless, the influent variability added a degree of reality to the experiment, where stormwater pollutant concentrations are expected to be highly variable. Large variation of fluoranthene has also been observed in actual stormwater measurements. Mansor et al. (2019) reported that fluoranthene concentrations in stormwater varied by a factor of 3336 from its lowest to highest values; Foster et al. (2000) observed stormwater fluoranthene variation of a factor of 223. Since the inflow and outflow concentrations both changed, fluctuation of removal was noted. Pyrene inflow connections ranged from 0.22 to 10.3 $\mu\text{g/L}$, chrysene ranged from 0.16 to 2.94 $\mu\text{g/L}$, benzo[a]anthracene ranged from 0.03 to 0.69 $\mu\text{g/L}$, and benzo[a]pyrene ranged from 0.03 to 0.57 $\mu\text{g/L}$. Fluoranthene outflow concentrations ranged from 0.0027 to 1.89 $\mu\text{g/L}$. The highest outflow concentration of 0.035 $\mu\text{g/L}$, 0.16 $\mu\text{g/L}$, and 0.067 $\mu\text{g/L}$, were noted for pyrene, chrysene, and benzo[a]anthracene, respectively, and all also have outflow concentrations < LOQ. All PAHs have less variation in outflow concentrations compared to input, indicating that the polishing columns can exhibit stable treatment performance on fluctuating PAH concentrations in stormwater. Fluoranthene, pyrene, and benzo[a]anthracene have limits for aquatic life in fresh water published by Canadian Council of Ministers of the Environment, except fluoranthene which have highest outflow concentration higher than the limit, other PAHs have all

concentrations lower than the limits. The removal of PAHs in this study also applied to the PAH concentrations in the realistic stormwater to estimate the performance of polishing treatment in practice, which discussed in detail in the following section.

Inflow and outflow PCB concentrations are shown in Fig. 3. Compared with PAHs, PCBs had less variation in inflow concentrations. PCB52 inflow concentrations ranged from 0.50 to 3.21 $\mu\text{g/L}$, PCB118 had the largest variation in the PCBs, which ranged from 0.10 to 5.68 $\mu\text{g/L}$. PCB138 and PCB180 ranged from 0.011 to 0.81 $\mu\text{g/L}$ and 0.036–1.91 $\mu\text{g/L}$ respectively. PCBs also exhibited less concentration variation in the outflow of polishing column, which shows that all polishing columns also provided stable treatment of PCBs. After treatment, PCB52 reduced to 0.0059–0.38 $\mu\text{g/L}$. The lowest discharge concentration for PCB118, PCB138, and PCB180 was < LOQ, and the highest concentration was 0.70, 0.11, and 0.39 $\mu\text{g/L}$, respectively. There is total PCB limit for aquatic life in the fresh water published by Maryland Department of the Environment. The total PCB limits cannot be applied to the individual PCBs in this study, however removals of PCBs in this study were applied to their represented PCB congeners based on Table S1, and PCB concentrations in the realistic stormwater were used to estimate the treatment efficiency of polishing treatment in practice. The detailed discussion is in the following section.

3.3. Removal of PAHs and PCBs

The results of PAH removal ($1 - C/C_0$) are shown in Table 3. The removal for all PAHs and PCBs fluctuated with time but did not have an overall increasing or decreasing trend (Figure S1 and Figure S2). All PAHs have removal >98.2% (benzo[a]anthracene) for all materials, and breakthrough was not observed for any of the materials. However, all materials demonstrated less fractional removal for PCBs, with a minimum removal of 75.9% for PCB180 on Biochar A. The PCB congeners demonstrated a decreasing trend of removal with increasing molecular weight. PCB180 had the lowest average removal of the 4 PCBs tested, which have removal <86.03%. The low removal of high molecular weight PCBs may result in low overall treatment performance when stormwater runoff contains a high concentration of high molecular weight PCBs (comparable to PCB180). As a result, for the practice of

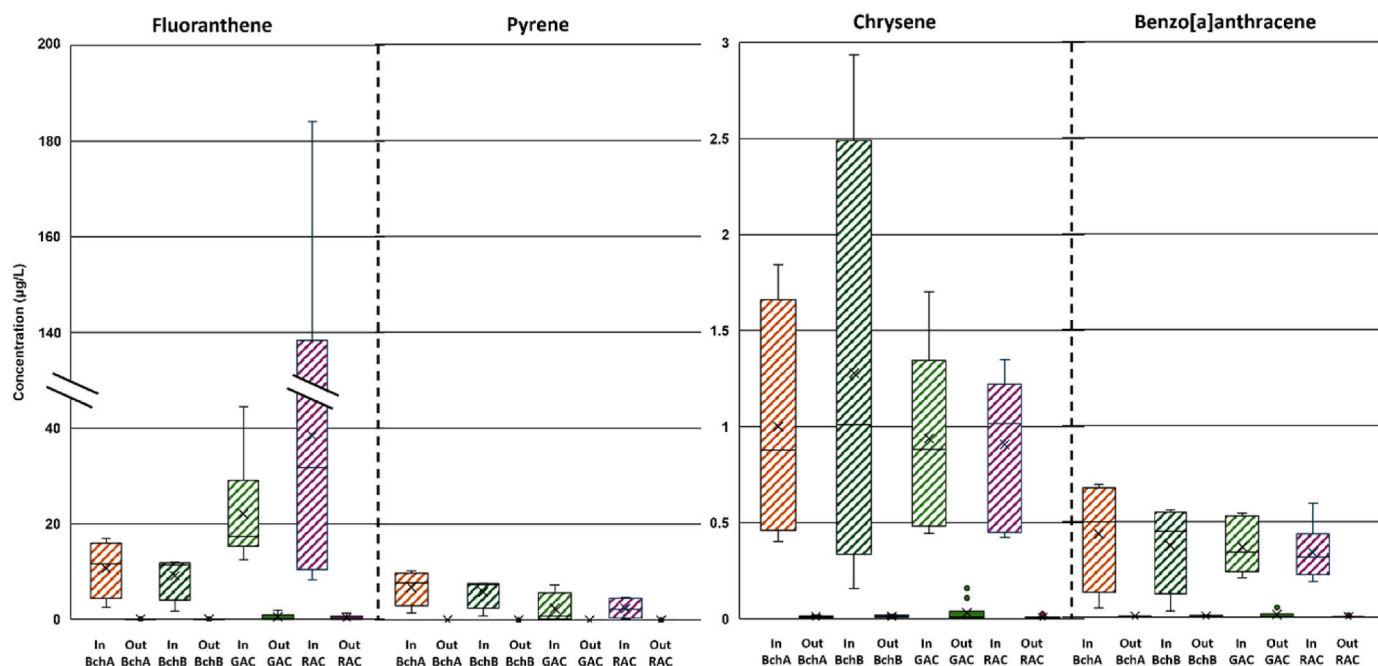


Fig. 2. PAH concentrations of influent and effluent samples. Chrysene and benzo[a]anthracene have less y-axis range compared with fluoranthene and pyrene, because they have lower concentration. The outflow columns are at the bottom of the figure, and still have a range of data.

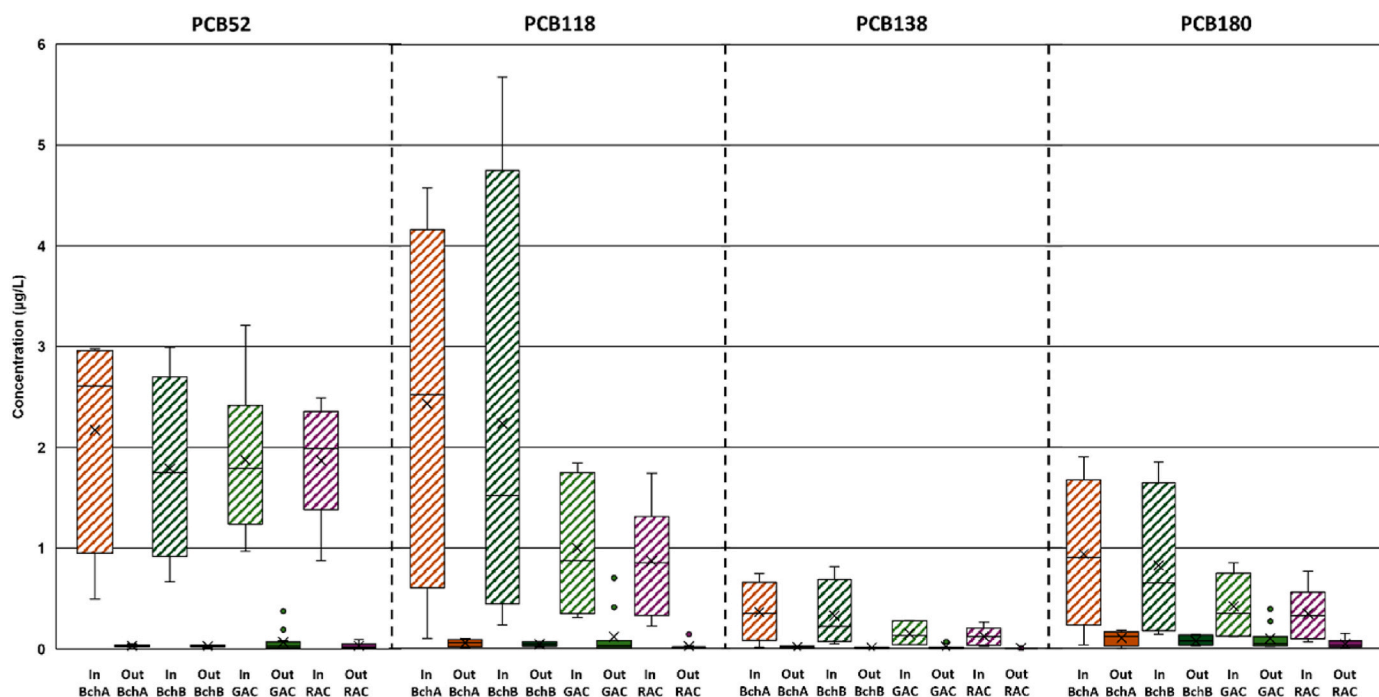


Fig. 3. PCB concentrations of influent and effluent samples. The outflow columns are at the bottom of the figure, and still have a range of data. The outliers were caused by the high outflow concentrations at 718 bed volumes.

Table 3
Removal efficiencies for PAHs and PCBs by tested polishing treatment media.

Compounds	BchA	BchB	GAC	RAC	Average
Fluoranthene	97.3%	99.5%	99.8%	99.8%	99.1 ± 1.2%
Pyrene	99.7%	99.8%	99.8%	99.7%	99.8 ± 0.1%
Benzo[a]anthracene	96.6%	99.4%	98.6%	98.2%	98.2 ± 1.2%
Chrysene	97.0%	99.4%	98.9%	99.1%	98.6 ± 1.1%
Average	97.7 ± 1.4%	99.5 ± 0.2%	99.3 ± 0.6%	99.2 ± 0.7%	
PCB52	96.4%	98.4%	98.6%	98.4%	97.9 ± 1.1%
PCB118	88.1%	97.3%	97.6%	98.2%	95.3 ± 4.8%
PCB138	87.4%	97.6%	96.3%	97.7%	94.8 ± 4.9%
PCB180	75.9%	87.7%	88.9%	91.6%	86.0 ± 6.9%
Average	87.0 ± 8.4%	95.3 ± 5.0%	95.3 ± 4.4%	96.5 ± 3.3%	

polishing treatment, PCB congener distribution in the stormwater runoff is an important consideration.

Biochar A had the lowest removal for both PAHs and PCBs, and other material had similar removal. PAH removal by Biochar A was significantly lower by biochar B (P-value = 0.04); other comparisons do not have significant differences. All materials did not have significant differences for PCB removal. Biochar A had the lowest surface area in of the adsorbent materials (237 m²/g), which may have influenced removal. Additional factors that may influence removal are discussed in the following section.

3.4. Concentration of PCBs on column media after treatment study

After the column experiment was completed, media from all the columns were divided into three parts, and PCBs and PAHs adsorbed onto the media were extracted. However, the recoveries of PAHs were <10% for all samples and only PCB concentrations are discussed (Fig. 4).

The bottom-up distribution of PCB concentrations was caused by the up-flow configuration of the synthetic stormwater; because the stormwater input was at the bottom of the columns, most PCBs were adsorbed by the media at the bottom of the columns. Media samples from the

bottom of the columns had the highest concentrations of all PCBs (PCB52: 1.26 ± 0.33 µg/g, PCB118: 0.81 ± 0.48 µg/g, PCB138: 0.10 ± 0.06 µg/g, PCB180: 0.23 ± 0.13 µg/g), and the mass percentages of accumulated PCB52, PCB118, PCB138, and PCB180 in bottom media to all media were 68.5 ± 18.5%, 74.3 ± 11.0%, 68.6 ± 9.4%, and 62.4 ± 8.6% respectively. BchA and BchB samples had the lowest PCB concentrations in the top samples. Some middle samples from GAC and RAC column had the lowest concentrations. The mass percentages of PCB52, PCB118, PCB138, and PCB180 in bottom media were 19.6 ± 14.7%, 14.8 ± 8.5%, 17.3 ± 6.9% and 19.9 ± 6.0% respectively. Although distribution of PAHs could not be assessed, it can be assumed that most PAHs also accumulated at the bottom of the column, because adsorption efficiency of PAHs was higher than PCBs. In addition, these results show that middle and top media still have adsorption capacity for PCBs, indicating that breakthrough and exhaustion did not take place during the experiment.

3.5. Discussion

The treatment efficiency was different among the PAH and PCB congeners. This may be caused by the molecular structure of the adsorbates and physical properties of the black carbon materials. Several factors influence adsorption of PAHs and PCBs on biochar and GAC. The first is the hydrophobicity (Mechlińska et al., 2009). Nam et al. (2014) studied the adsorptive removal of organic compounds in water with different K_{OW} and the results showed that log-scale sorption coefficients from Freundlich isotherms have a positive correlation with log K_{OW} of hydrophobic compounds. Therefore, organic pollutants with high K_{OW} values will have a higher affinity for sorption by polishing treatment in the media. In this study, PCBs have higher K_{OW} than PAHs, which would suggest greater removal efficiency of PCBs compared with PAHs if hydrophobicity is the dominant removal mechanism. However, the results show that PCBs have lower removal compared with PAHs (Fig. S3). PCB180 has the highest K_{OW}, but lowest removal (Table S2); therefore, other factors will influence the adsorption of these organic chemicals.

The second factor that can affect the adsorption is the molecular structure. Molecules with a planar structure can be adsorbed onto black

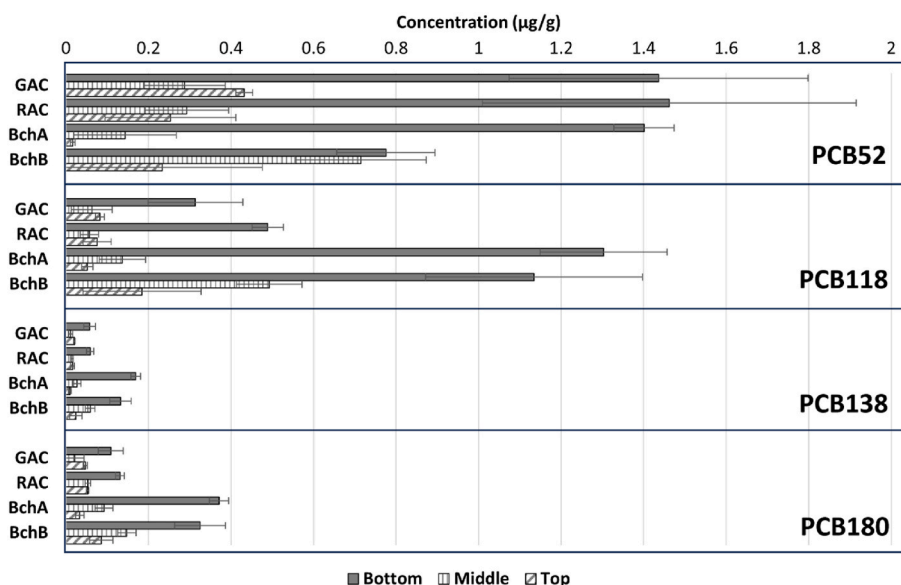


Fig. 4. PCB concentrations in the media after the completed column study, from bottom, middle, and top of the columns. Error bar shows the standard deviation of samples from three replicated columns.

carbon adsorbent surfaces by π - π electron donor and acceptor effects with aromatic rings on the biochar surface (Reguyal and Sarmah, 2018), which leads to a higher adsorption capability compared to the molecular without a planar structure (Sun and Zhou, 2008). PAHs with planar structures are easier to adsorb; the π - π complex can be formed between π -electrons of aromatic rings and active sites on the carbon surface (Eeshwarasinghe et al., 2019). Ge et al. (2015) studied the adsorption of phenanthrene and naphthalene on coal-based activated carbon in batch experiments, and results showed that phenanthrene (3 rings) was adsorbed to a greater extent than naphthalene (2 rings), which indicates that π - π effect increase with the number of aromatic rings on PAHs.

In some PCB congeners, due to the di-ortho substitution, the dihedral angle adjustment is limited. As a result, di-ortho substitution PCB congeners will form non-planar structures (Nuerla et al., 2013), and thus inhibit π - π bonding. Jonker et al. (2002) studied adsorption of PCBs on soot and soot-like materials, and the results showed preferential adsorption of PCBs with planar configurations. In this study PCB 52, PCB 138, and PCB 180 are di-ortho PCBs (Table S2), so their molecular structure is not conducive to the formation of π - π bond, which in turn reduces their tendency to be adsorbed by biochar and GAC. PCB118 does not have the di-ortho structure. A third factor is pore size distribution of the adsorbents and the corresponding relative molecular size of organics, since the pore size can limit the entry of larger molecules to specific sorption sites by steric hindrance; the larger molecules will be more difficult to be adsorbed by GAC and biochar (Wang et al., 2016). Molecules with larger molecular volume are more affected by steric hindrance, and di-ortho-substituted PCBs show more steric congestion than mono-ortho homologues (Llorca et al., 2020). Cornelissen et al. (2004) conducted a batch study examining the influence of steric hindrance on organic pollutant adsorption on black carbon, and results shows that steric hindrance strongly attenuates black carbon sorbate-interactions for nonplanar PCBs. In this study, PAHs removal was only moderately influenced by molecular size; pyrene and fluoanthrene have the lowest molecular size (186.0 Å³ and 187.7 Å³) (Hawker and Connell, 1988; Huckins et al., 1999) and highest removal (99.8% and 99.1%), chrysene and benzo[a]anthracene have higher molecular size (212.2 Å³ and 212.9 Å³) and lower removal (98.6% and 98.2%). PCBs also have increasing molecular size with increasing number of chlorine atoms (Table S2). Estimated molecular size increased from 230.1 Å³ (PCB52) to 284.2 Å³ (PCB180) (Hawker and Connell, 1988), and mean removal reduced from 97.9% to 86.0%.

Finally, DOM in stormwater will affect the adsorption of organic pollutants by clogging of pores, therefore, planar molecules will be affected more by DOM than non-planar molecules (Koelmans et al., 2009; Nuerla et al., 2013). McDonough et al. (2008) studied adsorption of PCBs on activated carbon in the presence of dissolved organic matter and biofilms, which reduced equilibrium adsorption capacity of PCB52 (water concentration was 10 ng/L) from 10³ to 10² ng/m². Koelmans et al. (2009) found that when 9.98 mg of humic acid/g of charcoal was loaded, the adsorption of PCB77 with a planar structure was reduced by 10 times, while the adsorption of PCB52 with a non-planar structure was reduced only by three times. Because PAHs have planar structure, PAH adsorption may be more influenced by the compost DOM than PCBs. The polishing columns were still able to provide >95% removal for PAHs with the added DOM. In this study, DOM may influence the adsorption of PAHs on biochar, because the BchA columns have significant lower PAH removal compared with other columns, and biochar columns have higher outflow TOC compare with AC columns, which may be caused by the additional leaching of DOM from biochar (Smith et al., 2016).

Evidence suggests that the adsorption performance of stormwater PAHs and PCBs on biochar and GAC was the result of the joint influence of the above factors. Overall, all PAHs demonstrated no breakthrough, and the low extraction recovery shows the desorption of PAHs was also limited; as a result, π - π bonds may be the most important factor in controlling PAH adsorption. This strong affinity also suggests that accumulated PAHs will not cause secondary pollution from the polishing treatment media.

The differences among different PCB congeners were more pronounced. PCB 118 has a planar structure, however the removal is low compared with PCB 52, which has a non-planar structure, so the number of chlorine substitutions may be the most important factor affecting the adsorption of PCBs. This is consistent with the results of PCB concentrations on the media; the proportion of PCBs adsorbed on the bottom media was reduced from 68.5% for PCB52 to 60.6% for PCB180 (Fig. 4), which shows that PCB congeners with higher molecular weight are less to adsorbed and thus less prone to accumulate in the media at the inlet.

Mercier et al. (2014) studied the adsorption of PCBs on F400, and the results indicated that GAC adsorbed tri- and tetra-CBs more efficiently than penta-CBs because of the higher steric hindrance of the penta-CBs. Jensen et al. (2011) studied the adsorption of PCB 77 and PCB 118 on GAC by software simulation; both PCBs were planar, so the planarity will not influence the adsorption. Results show that sufficiently small

pore size will hinder PCB 118 from entering. Pritchard et al. (2022) studied the transportation of organic pollutants in biochar and RAC columns; the results shows that the transport of organics in the column do not correlate with K_{ow} , and other factors such as molar volume and polar surface area may have more influence than K_{ow} . This result is consistent with this study.

Adsorption of PCB1 (planar) and PCB52 (non-planar) on GAC was studied by Sotelo et al. (2002) and fitting results of the kinetic model show that PCB1 has a higher macropore diffusivity than PCB52 ($9.03 \times 10^4 \text{ cm}^2\text{s}^{-1}$ compared to $3.2 \times 10^2 \text{ cm}^2\text{s}^{-1}$). Nollet et al. (2003) studied the adsorption kinetics of PCBs on fly ash, and the overall adsorption rate constant of PCB21 (mono-ortho substitution) was higher than PCB173 (tri-ortho substitution). These studies suggest that the rate of internal transport may be the limitation of high-chlorine substituted PCBs adsorption. The removal of PCB180 in this study was lower than other PCBs, and the fraction of PCBs in the bottom media samples to all media decreased with molecular weight, which may be caused by its slow diffusion on the adsorbent surface and in the pores of the absorbent (Lesage et al., 2010).

Therefore, when considering the use of GAC or biochar for stormwater polishing treatment, adsorption kinetics of highly chlorinated PCBs must be considered. The polishing treatment column requires sufficient retention time for adsorption, when stormwater runoff contains either high-chlorine substituted PCBs or multi-ortho-substituted PCBs. The retention time is necessary to allow for the adequate adsorption of PCBs.

Based on the mean removal of individual congeners, the estimated treatment performance for realistic stormwater was calculated (Table 4) based on the removals and the corresponding pollutants in real stormwater given in Table S1. Mean removal of the whole column experiment was calculated for each model pollutant. For PAHs, more than one model pollutant represented one group of realistic pollutants; the mean removal of fluoranthene and pyrene was used for MMW-PAHs, and mean removal of chrysene and benz[a]anthracene was used for HMW-PAHs. The formula used for the treatment calculation was:

$$C_{in} \times (1 - R) = C_{out} \quad (1)$$

where C_{in} indicates the pollutant concentrations in stormwater runoff, R represents the mean fractional removal of the model pollutants, and C_{out} represents the estimated outflow pollutant concentrations.

Because the treatment performance was calculated based on the

measured concentrations of pollutants in real stormwater, the results can be lower than MDLs employed in this study (Table 4). The results were compared with water quality criteria. Maryland Department of the Environment has a published PCB water quality criterion as total PCB concentration, so the individual PCB concentrations in Table 4 were summed to compare with the criterion. Canadian Council of Ministers of the Environment has published water quality criteria for some individual PAHs, which are listed and compared in Table 4. Using these assumptions, the polishing column can reduce the max PCB concentration in stormwater to lower than surface water limits, which indicate that use of the treatment of polishing columns will reduce total max PCB concentrations to values that will not pose risk for aquatic life. Fluorene will have a max concentration lower than the limit; anthracene and fluoranthene will only have the max concentrations above the limits. Pyrene, benzo[a]anthracene, and benzo[a]pyrene have median concentrations below limits. Which means that due to the high concentration of some PAHs in stormwater, polishing treatment will need to be combined with other SCMs to reduce PAH concentrations lower than these limits. To make the PAHs with max concentration below the limits, an additional 65–93% removal is needed. Assuming that the polishing treatment will be installed following another traditional SCMs, the fraction of PAHs adsorbed on particles will be removed before the polishing treatment. Hwang et al. (2006) studied distribution of PAHs in stormwater of Anacostia River, which showed that 68–97% of PAHs were distributed in the particle phase. As a result, combining the polishing treatment with traditional SCMs may have a better treatment performance in practice.

The mass loading of pollutants removed per area was estimated based on the 30-year (1992–2022) average annual precipitation for the U.S. northeast (115.6 cm/year) and northwest climate region (81.9 cm/year) (National Oceanic and Atmospheric Administration, 2023). Based on the assumptions used in the column design, total PAH mass removed was 194.0 g/(ha-yr) for the northeast and 274.0 g/(ha-yr) for the northwest. For PCBs, the removals are 0.87 g/(ha-yr) and 1.23 g/(ha-yr) for northeast and northwest, respectively.

Removal of other organic pollutants by biochar and GAC in stormwater was also studied. Parker et al. (2023) tasted removal of per- and polyfluorinated alkyl substances (PFAS) by biochar and GAC, and different material has a large variation of removal, the material with lowest removal removed 2–7% PFAS, and the material had highest removal with the range of 84–95%. Therefore, for the practice of realistic stormwater treatment, removal of all organic pollutants needs to be

Table 4

Estimated outflow concentration (based on measured concentrations) after completed polishing treatment compared with surface water standards. *BSM: Bioretention Soil Media.

Pollutants	Removal by *BSM	Concentration in stormwater runoff (ng/L)				Concentration in polishing treatment outflow (ng/L)				Aquatic life Criteria (ng/L)
		Min	Mean	Median	Max	Min	Mean	Median	Max	
≤4 Cl PCBs	97.9%	1.64			148	0.0344			3.11	
5 Cl PCBs	95.3%	2.83			39.7	0.133			1.87	
6 Cl PCBs	94.8%	3.2			13.8	0.166			0.718	
≥7 Cl PCBs	86.0%	2.08			9.11	0.291			1.28	
Total						0.625			6.97	14
Fluorene	99.4%	21	206	110	1190	0.126	1.24	0.657	7.14	3000
Phenanthrene	99.4%	17	2450	944	28800	0.102	14.7	5.66	173	
Anthracene	99.4%	42	534	199	5860	0.252	3.2	1.19	35.2	12
Fluoranthene	99.4%	11	4400	1590	36700	0.066	26.4	9.54	220	40
Pyrene	99.4%	10	3460	1250	29100	0.06	20.7	7.5	175	25
Benzo[a]anthracene	98.4%	20	1280	444	9840	0.32	20.5	7.1	157	18
Chrysene	98.4%	29	2200	1260	14700	0.464	35.1	20.1	235	
Benzo[b]fluoranthene	98.4%	55	3090	1830	18500	0.88	49.5	29.2	296	
Benzo[k]fluoranthene	98.4%	23	1440	884	7720	0.368	23	14.1	124	
Benzo[a]pyrene	98.4%	31	1890	766	13500	0.496	30.3	12.3	216	15
Dibenzo[a,h]anthracene	98.4%	75	581	527	1710	1.2	9.3	8.43	27.4	
Benzo[g,h,i]perylene	98.4%	24	1060	704	4970	0.384	17	11.3	79.5	
Indeno[1,2,3-c,d]pyrene	98.4%	184	1380	871	6230	2.94	22.1	13.9	99.7	

¹ Data source of PCB concentrations: Hwang et al. (2006), data source of PAH concentrations: Masoner et al. (2019). Blank indicates no data available.

² Surface water limit of total PCBs: Maryland Department of the Environment. Limits of PAHs: Canadian Council of Ministers of the Environment.

tested.

3.6. Estimation of polishing treatment media lifetime and cost

The lifetime and cost of the tested media used in an upscaled stormwater treatment facility were calculated (Table 5), and the calculation details are shown in the supplementary information (Formula Eq. S1 to Formula Eq. S7). The same 30-year average annual precipitation values were used for the U.S. northeast and northwest climate regions. In practice, a higher proportion of black carbon material will be used than in the study columns, to prolong the breakthrough time. Two media ratios were considered to reflect the impact of the amount of black carbon material, specifically 25% upscale (1:3 mass of media: sand), and 50% upscale (1:1 mass of media: sand). Since all polishing media used in this study did not breakthrough even at the last measurement point, the bed volume of the last point was used to calculate lifetime (383 bed volumes for biochar A and B, 886 bed volumes for GAC and RAC). As a result, all adsorbents used in this study have an effective long lifetime (Table 4) for PAHs and PCBs and can be used for the polishing treatment after conventional stormwater treatment.

Material prices were obtained in 2023 (Biochar Supreme Environmental Ultra, WA, Norit GAC 830R, and Calgon), which were AC \$262 m⁻³ (Biochar), \$763 m⁻³ (RAC), and \$1630 m⁻³ (GAC). Cost of black carbon material per hectare was calculated based on 50% upscale, 60-cm depth of polishing treatment facility, and 20:1 drainage area to treatment area ratio. The results showed the cost based on the last measurement point, and no material reached breakthrough, so the cost of material in practice should be lower than the results in Table 4. In this study, biochar A had significant lower treatment efficiency of PAHs compared with biochar B, which means that different biochar may not have stable treatment efficiency on organic pollutants, as a result, in the consideration of efficiency and cost, RAC is recommended for the polishing treatment.

4. Conclusion

In this study, PAHs and PCBs concentrations in synthetic stormwater before and after flowing through polishing treatment columns with biochar and activated carbon were assessed and removals were calculated. The results showed that PAH and PCB concentrations were reduced by more than 98% and 86% for synthetic stormwater by all columns, and outflow concentrations had lower variation compared with inflow concentration, which means that the polishing treatment can have high stability on the treatment effect. All PAH concentrations were removed >98% (Benzo[a]anthracene was removed by 98.2 ± 1.2%, and mean concentration was reduced from 0.38 ± 0.041 µg/L to 0.0068 ± 0.0042 µg/L). Removal of PCBs were higher than 86% (PCB180 was removed by 86.0 ± 6.9%, mean concentration was reduced from 0.63 ± 0.29 µg/L to 0.079 ± 0.029 µg/L).

Removal mechanisms were limited by the molecular structure, and PCB180 which have the non-planar structure and largest molecular size had the lowest removal, therefore for the practice of polishing treatment with black carbon material, the molecular structure of organic pollutants in the stormwater need to be considered. If there are high concentration of organic pollutants in the stormwater, more black material may be needed in the polishing treatment facility to improve treatment efficiency.

Removal of PCBs reduced with increasing PCB molecular weight. Therefore, when considering the practical application of a polishing treatment, high molecular weight PCBs should receive priority attention because the adsorption of high molecular weight PCBs had lower removal efficiency and may have faster breakthrough. If the stormwater contains a high concentration of high molecular weight PCBs, the content of the adsorbent in the media can be increased.

A media lifetime calculation indicated that all media had lifetimes

Table 5

Media lifetime and estimated costs for upscaled conditions. Maryland and Washington are used as examples for different climate and precipitation zones.

Media	Maryland		Cost (\$/(ha-yr))	Washington		Cost (\$/(ha-yr))
	25% upscale (years)	50% upscale (years)		25% upscale (years)	50% upscale (years)	
BchA	>29	>36	< \$1878	>41	>51	< \$1332
BchB	>29	>36	< \$1878	>41	>51	< \$1332
GAC	>96	>147	< \$2658	>135	>206	< \$1884
RAC	>96	>147	< \$1137	>135	>206	< \$804

>29 years when used for an upscale polishing treatment practice. Since most organic pollutants accumulate in the media at the inflow, the lifetime of the media can be extended by replacing the media at the inflow. Based on the efficiency and cost calculation, RAC is recommended for stormwater polishing treatment.

CRediT authorship contribution statement

Chen Yuan: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Kristen Croft:** Writing – review & editing, Methodology, Data curation. **Sabrina de Nicola:** Methodology, Data curation. **Allen P. Davis:** Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization. **Birthe V. Kjellerup:** Writing – review & editing, Visualization, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2025.144107>.

Data availability

Data will be made available on request.

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