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Evaluation of Sorbents and Matrix Effects for Treating Heavy Metals and Per- and Polyfluoroalkyl Substances as Co-Contaminants in Stormwater

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Heavy metals and per- and polyfluorinated alkyl substances (PFAS) are both contaminants regularly found in stormwater; however, their different properties make them challenging to treat together. In this study, we use multiple sorbents that combine hydrophobic and anion exchange retention mechanisms while minimizing matrix effects, resulting in greater overall removal of heavy metals and PFAS in stormwater.

ARTICLE

Evaluation of Sorbents and Matrix Effects for Treating Heavy Metals and Per- and Polyfluoroalkyl Substances as Co-Contaminants in Stormwater

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Heavy metals and per- and polyfluoroalkyl substances (PFAS) are two classes of contaminants of environmental and toxicological concern that are found in stormwater. There are limited studies that address their treatment when they occur together as co-contaminants. The objective of this study was to evaluate four commercially available sorbents (Biochar Basic, EarthLite, RemBind™, and Calgon F400) for the removal of heavy metals and PFAS from stormwater. A series of synthetic and field-collected stormwaters were used to inform sorbent selection. Due to the significant differences in the chemical properties of heavy metals and PFAS, a series of sorbents (*i.e.*, a treatment train) was selected for optimal removal. Real stormwater collected from the Oregon State University Benton County Green Stormwater Infrastructure Research (OGSIR) facility was characterized in order to determine which matrix components impact sorbent performance. Organic matter in real stormwater significantly decreased PFAS removal efficiencies by RemBind™ from 84-95% to 0-45%. Pretreating OGSIR stormwater with Biochar Basic removed suspended solids and resulted in significantly greater removal (20-60% increases) for eleven out of twenty-one PFAS. The final sorbents selected for stormwater treatment were Biochar Basic, which is first deployed for heavy metal removal, followed by RemBind™ for PFAS removal.

1. Introduction

Heavy metals and per- and polyfluoroalkyl substances (PFAS) are two classes of environmental contaminants regularly found in stormwater runoff, which may contaminate nearby bodies of water or receiving sediments, resulting in negative environmental and health impacts.¹⁻³ Copper and zinc are bioaccumulative and toxic to many plant and aquatic species.^{4,5} A number of well-studied PFAS, namely perfluorooctanoic sulfonic acid (PFOS), perfluorononanoic acid (PFNA), and perfluorohexane sulfonic acid (PFHxS), are linked to liver and kidney toxicity in humans and animals.⁶ There are a number of places in which there are sources of both heavy metals and PFAS resulting in the co-occurrence of these contaminants in stormwater. For example, copper and zinc can be found in brake dust, galvanized fencing, and roofing material at military sites.⁷ A wider range of PFAS are found in aqueous film forming foams that

were historically stored, handled, and applied at military firefighter-training sites.⁸

While both classes of contaminants are of environmental concern, their unique properties affect their fate and transport in the environment very differently. Heavy metals carry positive charges and are readily adsorbed to soils or particulate matter; however, they are dependent on redox chemistry and can be also be readily desorbed from soils or particulate matter.^{9,10} In contrast, PFAS are generally characterized by a hydrophobic, fluorinated tail attached to a hydrophilic, charged head group.¹¹ The most well-studied PFAS are anionic under environmental conditions, which contributes to their high water solubility and high rates of transport through soil and into groundwater.¹²

Although heavy metals and PFAS are common stormwater co-contaminants, there are limited studies addressing their simultaneous treatment, which is likely due to the challenges presented by their differing sorption and transport properties. Additionally, a majority of stormwater studies use synthetic stormwater, which may not represent the complexity of actual stormwater.¹³ As a result, relatively little information is available on

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how stormwater constituents potentially affect the co-treatment of heavy metals and PFAS by sorbents.

Sorbents are an appealing remediation technique as they are relatively low-cost compared to other treatment techniques (e.g., nanofiltration and electrochemical oxidation).^{14, 15} Carbon-based sorbents in particular, including biochar and granular activated carbon (GAC), are commonly used to treat heavy metals or PFAS in stormwater,¹⁶⁻¹⁸ but are rarely studied to remove both broad classes of contaminants simultaneously. However, a limitation with biochar and GAC is that they are not selective and their effectiveness for removing heavy metals and PFAS is reduced in complex matrices.¹⁹

In contrast, anion exchange sorbents are much more selective than GAC, especially for shorter-chain, anionic PFAS, leading to the popularity of GAC-based sorbents that have anion exchange capacity, such as RemBind™.²⁰ However, while popular in groundwater and drinking water treatment systems,^{21, 22} the effectiveness of sorbents with anion-exchange capacities in more complex aqueous matrices, such as stormwater treatment systems, is still unknown.

The objective of this study was to compare sorbents for the removal of heavy metals (copper and zinc) and PFAS, including select perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFASs), from stormwater to inform sorbent selection for use at a field demonstration site. Four sorbents, including two biochars and two GACs, with varying degrees of ion exchange capacities, were compared in batch experiments for their removal of heavy metals (copper and zinc) and three PFAS: PFHxS, PFOS, and perfluorooctanoic acid (PFOA). Sorbents were then screened using single-point batch sorption experiments with synthetic and field-collected stormwater to determine the best sorbent for removal of each constituent. Stormwater was characterized and major components (e.g., salts, iron, and organic matter) were evaluated for their impact on sorbent performance. The effect of stormwater matrix components on sorbent performance were then used to inform the order of sorbents for a treatment train remediation approach. Finally, the sorbent order was validated with a broad suite of twenty-one anionic PFAS including PFCAs, PFASs, perfluoroalkyl sulfonamides, chlorinated PFAS, hexafluoropropylene oxide dimer acid (HFPO-DA) and sodium dodecafluoro-3H-4,8-dioxanonanoate (NaDONA).

2. Experimental

2.1 Materials

2.1.1 Chemicals. Heavy metals, including copper and zinc, were purchased as aqueous solutions from VWR (Radnor, PA). Iron was purchased as a powder from VWR (Radnor, PA) for use in synthetic stormwater. A standard of PFOA (95%) was purchased as the free acid and PFHxS (98%) and PFOS (98%) were purchased as salts from Sigma-Aldrich (Milwaukee, WI). Thirteen isotopically labelled PFAS and 18 additional native PFAS including eight perfluoroalkyl

carboxylic acids (PFCAs), six perfluoroalkylsulfonic acids (PFASs), two perfluoroalkyl sulfonamides, two chlorinated PFAS, perfluoroethylcyclohexane sulfonate (PFEtCHxS), dodecafluoro-3H-4,8-dioxanonanoate (ADONA), and 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoro propoxy)-propanoic acid (HFPO-DA, Table S1) were purchased as solutions from Wellington Laboratories (Ontario, CAN).

2.1.2 Sorbents. Biochar Basic, a 100% Douglas fir biochar blended with activated ceramic, was donated by Stormwater Biochar (Eugene, OR). EarthLite was purchased from SunMark Environmental (Clackamas, OR) and is a biochar blend made from hazelnuts. Calgon F400 was donated by Calgon Carbon Corporation (Moon Township, PA) and is an activated carbon made from bituminous coal. Calgon F400 was added as a benchmark sorbent because it is currently being used as some impacted DoD sites. RemBind™ was donated by Ziltek (Thebarton, Australia) and is a blend of GAC, aluminum hydroxide, and kaolite clay and has a net positive charge capable of anion exchange.²³ The cation exchange capacity (CEC), pH, and organic carbon (measured by proxy as loss on ignition), were determined for each sorbent using the methods laid out in Gavlak et al.²⁴

2.1.3 Stormwaters. The *Simple Synthetic* stormwater consisted of nanopure water adjusted to pH 6 with the addition of 0.185 mM NaHCO₃ and 1.0 mM NaCl (Table S2). Two complex synthetic stormwaters were made to simulate versions of OGSIR SW, one with the same inorganic (e.g., ammonia, phosphate, chloride, sulfate, nitrate) composition (*Complex Synthetic*), but without organic matter and iron and a second version that also contained iron (*Complex Synthetic with Iron*), but no organic matter (Table S2).

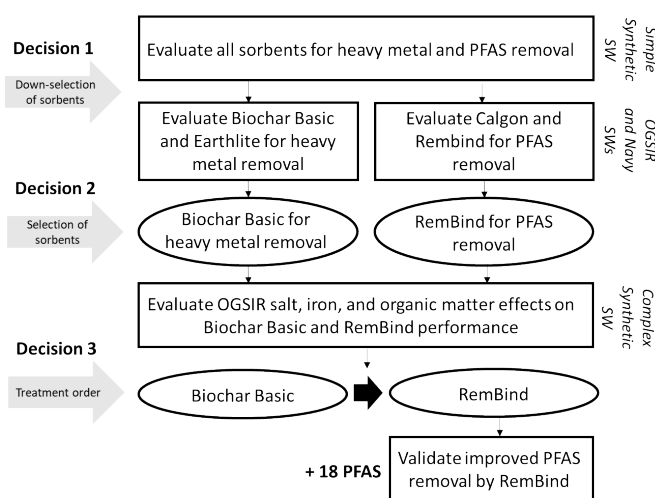
Stormwater (OGSIR SW) was collected from the Oregon State University Benton County Green Stormwater Infrastructure Research (OGSIR) facility, an established onsite bioswale used to study the treatment of stormwater (Table S2).^{23, 24} Treated OGSIR SW (Table S3) was created by running OGSIR SW through a Biochar Basic column. The Biochar column was 1.27 cm in diameter with a cross sectional area of 1.27 cm² and length of 12.45 cm. The porosity of Biochar Basic was 0.460 and the average particle diameter of 0.585 mm. The flow rate was 0.25 mL/min, resulting in a contact time of 29.2 min. A second field-collected stormwater was obtained from a PFAS-impacted Navy site (Navy SW) and was included as secondary source of stormwater to prevent sorbent selection from becoming too site specific.

2.2 Batch Experiment Workflow

A series of batch experiments were conducted to evaluate the performance of four individual sorbents and then to determine the order of the selected sorbents in a treatment train (Figure 1). Biochar Basic, EarthLite, Calgon F400, and RemBind™ were evaluated for heavy metal and PFAS removal using the simple synthetic stormwater. Sorbents that were ineffective at removing heavy metal or PFAS in the *Simple Synthetic* stormwater matrix were eliminated from further investigation (Figure 1, Decision 1).

Sorbents that gave the greatest removal of heavy metals and/or PFAS were then evaluated using two real stormwaters (OGSIR SW and Navy SW) (Figure 1, Decision 2). The best performing sorbent for heavy metals and PFAS removal from field-collected stormwaters were then examined to determine the impact of salts and iron (Figure 1, Decision 3) using *Complex Synthetic* (salts only) and *Complex Synthetic w/Iron*. The effect of organic matter on sorbent performance was inferred from the difference observed between *Complex Synthetic w/Iron* and that of collected OGSIR SW (contains organic matter; Table S2).

Figure 1. Workflow of batch experiments and decision points for selecting sorbents using various stormwaters (Table S2) for the removal of heavy metals (copper and zinc) and three model PFAS.



To validate sorbent order in a treatment train, the performance of Rembind™ was evaluated with untreated OGSIR SW and OGSIR SW that had been pre-treated by passing it through a Biochar Basic column, as described above (see 2.1.3). Following pretreatment, 21 PFAS (full list of target PFAS in Table S1) were added to the pre-treated OGSIR SW and removal by Rembind™ was quantified in batch experiments (see below).

2.3 Batch Experiment Protocols

All single-point batch experiments for metals and PFAS removal were conducted separately. All batch experiments were performed with a minimum of three replicates. Three model PFAS (PFOA, PFHxS, and PFOS) were used for the screening and selection of sorbents (Decisions 1 and 2). For the validation of selected treatment (Decision 3), a total of 21 PFAS were used to find percent removal of PFAS by RemBind from OGSIR SW with and without Biochar Basic pretreatment. Either metals (200 µg/L zinc and 50 µg/L copper) or native PFAS (1,000 ng/L of each compound) were spiked into HDPE bottles containing a constant ratio of sorbent (e.g., Biochar Basic, EarthLite, etc.) to stormwater of 50mg:25mL for heavy metals and 5mg:125mL for PFAS. The bottles were homogenized and shaken for 24 h in a tumbler and aliquots were collected at 0 h and 24 h. Previous batch studies observed that

equilibrium times between PFAS and some soils/sorbents may be as long as 3 weeks.^{25, 26} It is unlikely that hydraulic retention times will ever allow for true equilibrium, thus, 24 h was selected as it a representative hydraulic retention time of the OGSIR bioswale. Heavy metal samples were filtered through a 0.45 µm syringe and 1 mL was preserved in 5 mL of 2% nitric acid in a 15 mL acid washed HDPE tube. All PFAS samples were centrifuged for 10 min at 25,000 G, and then a 1.5 mL aliquot was transferred to an autosampler vial and spiked with an isotopically labelled surrogate standard (Table S1) to account for instrument variability. Controls consisted of spiking each stormwater matrix with the same level of metals or native PFAS, but with no sorbent present.

2.4 Analytical Analysis

2.4.1 Instrumental Analysis. Copper, zinc, and iron analyses were performed with a ThermoScientific iCAP RQ using EPA method 200.7.²⁷ The PFAS analysis was adapted from Rewerts et al 2021.²⁸ Briefly, aqueous samples were introduced via large-volume aqueous injections onto a high-performance liquid chromatograph fitted with C18 guard and analytical columns with detection by a triple quadrupole mass spectrometer (HPLC-TQD-MS). Full details of HPLC-TQD-MS method and instrumental settings can be found in the SI.

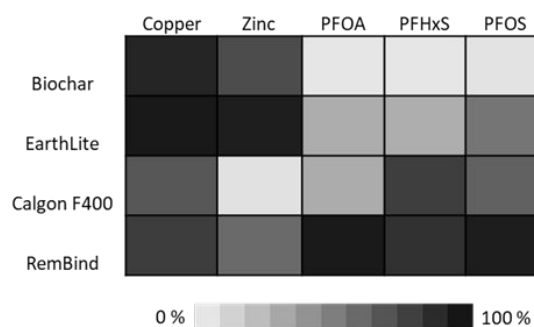
2.4.2. Statistical Analysis. T-tests and one-way Anova with post-hoc Tukey tests were performed to compare percent removals between sorbents for batch experiments.

3. Results and Discussion

3.1 Sorbent Screening in Simple Synthetic Stormwater

To screen for sorbents suitable for removing heavy metals or PFAS from stormwater, the performance of the four initial sorbents was evaluated using *Simple Synthetic* stormwater (Figure 1) in single-point batch tests. Biochar Basic and EarthLite resulted in greater removals of copper and zinc (75-99%) than Rembind™ (60-82%; Figure 2, Table S4). Calgon F400 gave the poorest removal of heavy metals with 69% for copper, and little to no removal of zinc.

Figure 2. Heatmap depicting the percent removal of copper and zinc and three model PFAS by four sorbents in batch tests with *Simple Synthetic* stormwater (n = 3). All data shown in Table S3.



Calgon F400 had the second greatest CEC (268 meq/kg; Table 1), but the lowest heavy metal removal. Thus, cation exchange capacities alone could not account for the differences between heavy metal removals from *Simple Synthetic* stormwater. This indicated that there are additional mechanisms responsible for heavy metal sorption. For example, the two biochar-based sorbents (Biochar Basic and EarthLite) removed greater amounts of heavy metals compared to the two GAC-based sorbents (Calgon F400 and RemBind™). The increased heavy metal removal by biochar-based sorbents may be attributed to surface complexation, an established retention mechanism of heavy metals by biochars due to their more abundant surface functional groups relative to GACs.²⁹⁻³¹

Of the four sorbents, the two that were made of GAC (Calgon F400 and RemBind™) demonstrated greater PFAS removal than the two biochar sorbents (Biochar Basic and EarthLite). Biochar Basic gave particularly poor removal (<10%) of PFOA, PFHxS, and PFOS (Figure 2, Table S4). Among the biochar sorbents, EarthLite was notably better than Biochar Basic, with 28-55% PFAS removal efficiencies compare to Biochar Basic's 2-7% PFAS removal efficiencies. In contrast, Calgon F400 and RemBind™ gave much greater removal efficiencies ranging from 28-81% and 84-95%, respectively. Previous studies have reported mixed results with GAC and biochar with some studies reporting more effective removal of PFOA and PFOS by GAC than biochar,²⁶ particularly in the presence of organic matter,³² while others report biochar performing as well or better than GAC.²⁵

After evaluation of heavy metals and PFAS removal, it was evident that no single sorbent would be effective for removal both heavy metals and PFAS. For this reason, two sorbents were needed. To select the best heavy metal sorbent, Biochar Basic and EarthLite were carried forward for heavy metal removal while Calgon F400 and RemBind™ were carried forward for PFAS removal from OGSIR SW and Navy SW.

3.2 Down-selected Sorbent Performance in OGSIR and Navy Stormwaters

Copper was removed more efficiently than zinc, with no statistical differences in removal from OGSIR SW or Navy SW by EarthLite and Biochar Basic (Table 1). Biochar Basic removed 78% and 74% of zinc from OGSIR SW and Navy SW, respectively, while EarthLite gave significantly lower removals of zinc from OGSIR SW (68%, p-value = 0.0376) and similar removal from Navy SW (72%, p-value = 0.1728; Table 1). Moving forward, Biochar Basic was selected for heavy metal removal due to its greater removal of zinc in OGSIR SW and Navy SW (Decision 2).

The relative performance of Biochar Basic and EarthLite for heavy metal removal from OGSIR SW (Table 1) was not expected from experiments based on *Simple Synthetic* stormwater (Figure 1). For instance, EarthLite removed greater amounts of zinc than Biochar Basic from *Simple Synthetic* stormwater, but Biochar Basic removed

greater amounts of zinc in OGSIR SW and Navy SW. The difference in relative sorbent performance between *Simple Synthetic* stormwater and field-collected stormwaters indicate that synthetic stormwater may not a suitable matrix for comparing and selecting sorbents for heavy metal removal.

Table 1. Percent removal of copper and zinc by Biochar Basic and EarthLite in field collected stormwaters (n = 3).

	Biochar Basic	EarthLite	p-value
OGSIR SW	<i>Average ± 95 CI</i>		
Copper	67 ± 11	83 ± 3	0.0683
Zinc	78 ± 4	67 ± 5	0.0376
Navy SW	<i>Average ± 95 CI</i>		
Copper	98 ± 2	95 ± 6	0.4818
Zinc	74 ± 5	72 ± 4	0.1728

There are many potential retention mechanisms for heavy metals by biochar (e.g., complexation, cation exchange).^{33, 34} EarthLite had a greater percentage of organic carbon (62.5% vs 55.5%, Table 2) and a lower CEC (187 meq/kg vs. 709 meq/kg) relative to Biochar Basic. Thus, it was speculated that retention via adsorption was more prominent in the synthetic stormwater while cation exchange was more important in real stormwaters containing organic matter. It is also possible that EarthLite has a higher adsorption capacity for all of the contaminants and components in real stormwater but is predominately due to hydrophobic interactions and is less selective than Biochar Basic for heavy metals like zinc. Additionally, it is possible that the co-occurrence of PFAS and heavy metals could result in increased retention of heavy metals due to interactions between anionic PFAS head groups and cationic heavy metals. Given the high CECs of Biochar Basic and EarthLite, increases to CECs due to PFAS adsorption may not occur in environmental conditions, but this could be of interest for further study.

Table 2. Cation exchange capacity (CEC), pH, and organic carbon content of each sorbent. Organic carbon was measured as loss upon ignition.

	CEC (meq/kg)	pH	Organic carbon (g/g)
Biochar Basic	709	6.01	55.5
EarthLite	187	9.47	62.6
Calgon F400	268	9.76	28.8
RemBind™	20.1	8.59	8.62

For PFAS, Calgon F400 and RemBind™ were evaluated with OGSIR SW and Navy SW. RemBind™ removed greater amounts of all three PFAS in both stormwaters (Table 3). Both Calgon F400 and RemBind™ performed better with Navy SW compared to the OGSIR SW. Calculations for percent removal of PFAS by Calgon F400 in OGSIR SW resulted in negative values. This is speculated to be due to fast initial sorption of PFAS to the Calgon F400 at time 0, when the sorbent was introduced, but desorption over the 24 hours

resulting in more PFAS present in the SW at the final timepoint relative to the initial. This was not further explored because RemBind™ was ultimately selected as the final sorbent for PFAS.

Table 3. Percent removal of PFOA, PFHxS, and PFOS by Calgon F400 and RemBind™ in field collected stormwaters (n = 3).

	Calgon F400	RemBind™	p-value
OGSIR SW	Average ± 95 CI		
PFOA	-13 ± 19	13 ± 17	0.0944
PFHxS	-15 ± 9	1.1 ± 13	0.0990
PFOS	-15 ± 17	45 ± 13	0.0015
Navy SW	Average ± 95 CI		
PFOA	1.8 ± 14	35 ± 3	0.0044
PFHxS	18 ± 8	31 ± 3	0.0218
PFOS	14 ± 8	65 ± 4	0.0001

Calgon F400 is a GAC that adsorbs PFAS via hydrophobic interactions,³⁵ while RemBind™ is a GAC blended with kaolite clay, which has a net positive charge that gives RemBind™ anion exchange capacity, and thus the capability to retain PFAS via hydrophobic and electrostatic interactions.²³ The relative contributions of these interactions are discussed more later, but the dual retention mechanisms present in RemBind™ are likely responsible for better performance in more complex matrices like OGSIR SW and Navy SW. Given the superior performance of RemBind™ in *Simple Synthetic* and field-collected stormwaters, it was selected as the sorbent for PFAS removal (Decision 2).

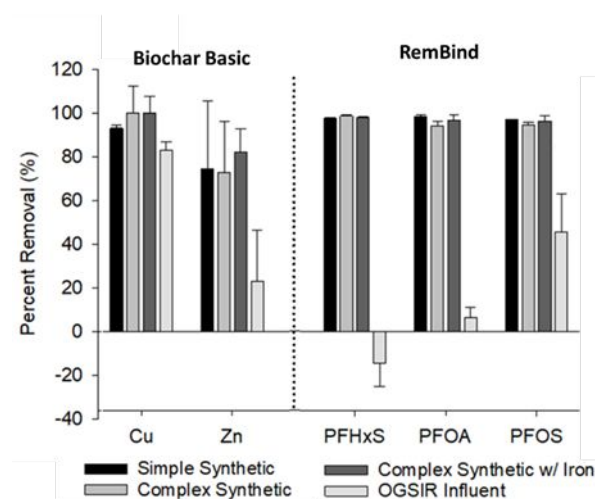
3.3 Matrix Effects of Stormwater on Sorbent Performance

Both Biochar Basic and RemBind™ gave decreased performance in heavy metal and PFAS removal from untreated OGSIR SW compared to *Simple Synthetic* stormwater (Figure 3). This suggests that OGSIR SW constituents inhibit the sorbents' performance. Chemical characterization of OGSIR SW revealed three main components: salts, iron (at a relatively large concentration of 210 µg/L), and organic matter (Table S2). This contrasts with *Simple Synthetic* stormwater, which is comprised of only sodium, chloride, and carbonates.

The *Complex Synthetic* stormwater, which includes additional salts and is similar to synthetic stormwaters that are commonly used,³⁶⁻³⁸ demonstrated no significant differences in sorbent performance at retaining either heavy metals or PFAS. In fact, the only stormwater component that resulted in significant decreases in heavy metals or PFAS removal was organic matter (Figure 3). In the case of metals, zinc was more sensitive than copper to changes in matrix composition, which is consistent with previous reports.³⁹ Additionally, organic matter had a more significant impact on reducing PFAS removal relative to heavy metals. The organic matter in OGSIR SW was comprised of dissolved organic matter (DOC), dissolved solids, and suspended sediment (Table S3). While DOC composition among environmental stormwaters likely varies, it is comprised of hydrophobic alkanes and anionic functional groups

(e.g., carboxylic acids).⁴⁰ Components of the DOC could potentially compete with PFAS for retention on RemBind™ via hydrophobic⁴¹ or anion exchange mechanisms.⁴² In addition to chemical competition between DOC and PFAS on RemBind™, there is also the potential for physical blockage caused by suspended sediment. The higher temperatures used to create GAC (as compared to biochar) result in smaller pores that can be clogged by suspended sediment.⁴³

Figure 3. Matrix effects of stormwater on Biochar Basic and RemBind removal of copper, zinc, and three PFAS (n = 3).



A practical consideration for sorbent remediation strategies is the cost associated with upkeep, such as the replacement frequency of sorbents due to heavy metals or PFAS breakthrough as well as the disposal of the used sorbents. High levels of contaminants or organic matter (e.g., suspended sediment, dissolved solids, dissolved organic carbon) can lead to earlier breakthrough of heavy metals and PFAS, which requires an increased frequency of replacement.⁴⁴ For treatments that require two or more sorbents, such as the co-removal of heavy metals and PFAS, stormwater matrix components won't necessarily impact both sorbents equally. Thus, the relative impact of stormwater matrices on sorbents was used to inform the order of sorbents in order to potentially minimize the need for sorbent replacement.

3.4 Validation of Treatment Order

To determine the optimal order of sorbents for a field-scale treatment train, RemBind™ was evaluated by first treating OGSIR SW with Biochar Basic. When OGSIR SW was pre-treated with Biochar Basic, RemBind™ demonstrated significant (p-value ≤ 0.05) increases in removal (20-60%) for 11 of the more hydrophobic PFAS (Figure 4; Table S5).

In general, RemBind™ demonstrated greater removal of PFAS from OGSIR SW as hydrophobicity increased (i.e., longer chromatographic retention times; Figure 4). Two notable exceptions to this are FHxSA and FOSA, which are perfluorinated sulfonamides. The pKa's of FHxSA and FOSA are ~6.2,⁴⁵ and the pH in OGSIR

stormwater ranges from 7.3 (no pretreatment) to 6.7 (with pretreatment; Table S3). Thus, FHxSA and FOSA are expected to be present both in their neutral and anionic forms. The greater percent removal of FHxSA and FOSA compared to PFCAs and PFASs with similar chromatographic retention times (e.g., PFOS, PFNA) indicate that hydrophobic interactions between the neutral species with the RemBind surfaces may be more dominant than the electrostatic/hydrophobic interactions of the anionic PFAS.

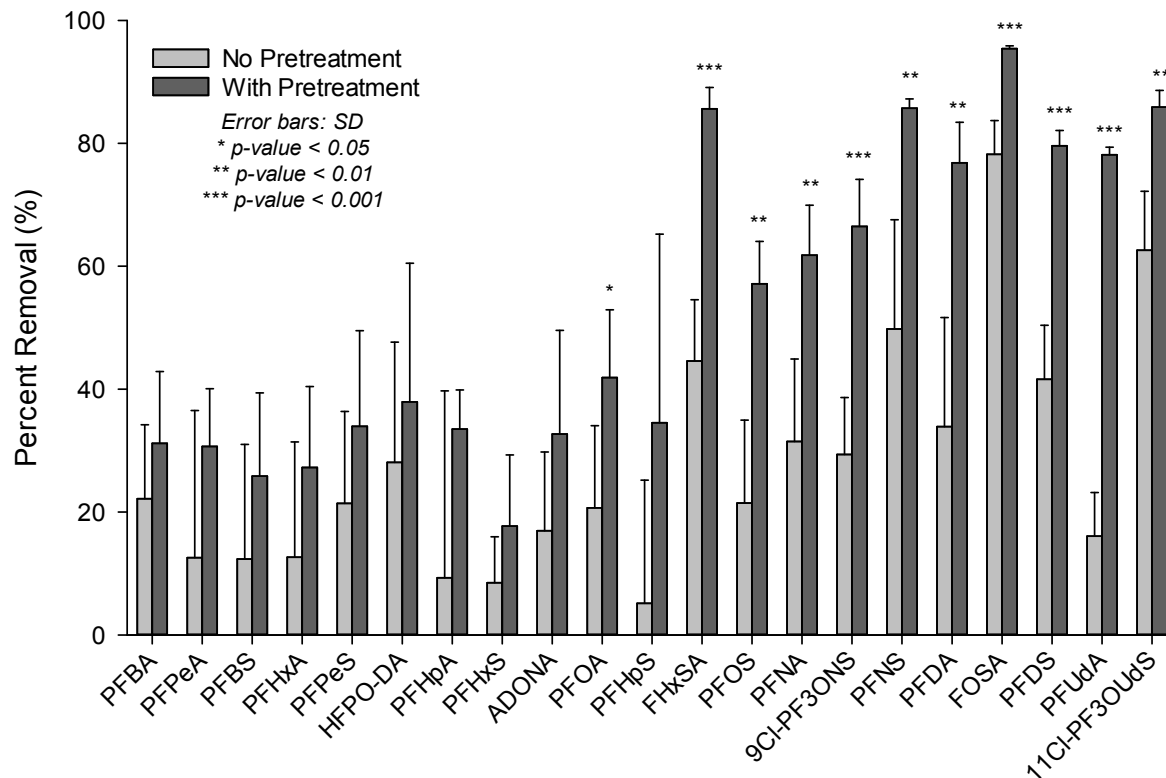
We previously demonstrated that a comparison in retention/removal among a homologous series (e.g., PFCAs) is useful in elucidating relative retention mechanisms in anion exchange sorbents.⁴⁶ If either electrostatic or hydrophobic interactions were occurring in isolation, a negative or positive slope, respectively, would occur when comparing retention across a homologous series. Conversely, if electrostatic and hydrophobic interactions are both occurring, a hockey-stick shaped curve is expected (i.e., intermediate chain lengths have lower removals than short and long chain homologs).

For OGSIR SW with no pretreatment, a hockey-stick curve was not observed (Figure S1). Additionally, a linear regression among PFCAs

resulted in a slightly negative slope, but there was no significant correlation ($p > 0.05$). In contrast, the hockey-stock curve was observed for OGSIR SW with pretreatment (Figure 5). The overall removal for all PFCAs increased with pretreatment, but the relative increased removal was much greater for PFCAs with 7 or more fluorinated carbons. The change in curve from a relatively flat line to a hockey-stick shape indicated that the increased retention of PFAS by RemBind™ was due primarily to an increase in hydrophobic interactions.

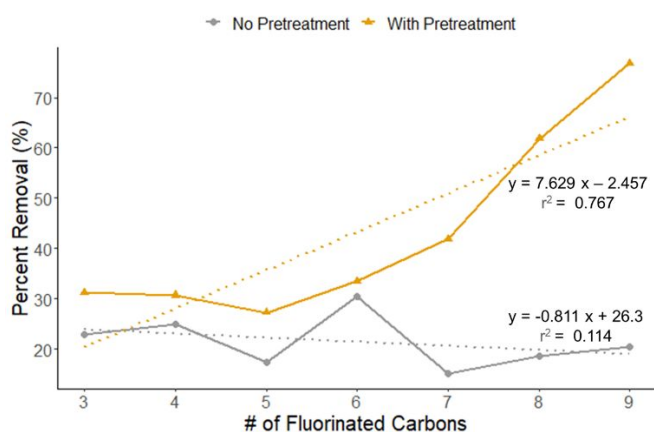
As discussed above, DOC in stormwater is typically comprised of mostly hydrophobic components.⁴⁰ Since biochars are generally effective at removing DOC from contaminated waters, it was initially speculated that pre-treating stormwater with Biochar Basic would result in greater PFAS removal because there would be less competition with DOC.⁴⁷ However, OGSIR SW that was characterized before and after pretreatment with Biochar Basic demonstrated no significant differences in DOC concentration (Table S3).

Figure 4. Removal of 21 PFAS by RemBind™ from untreated and pre-treated OGSIR SW. Analytes are ordered based on increasing retention time on a C18 analytical column ($n = 4$). All data shown in Table S5.



Conversely, the Biochar Basic was effective at removal of both suspended sediment (76% removal) and iron (87% removal) from OGSIR SW. When tested systematically, the presence of iron in synthetic SW did not previously impact PFAS removal (Figure 3). Thus, the presence of suspended sediment was the most likely component in OGSIR SW that reduced PFAS removal by RemBind™. Physical pore blockages from suspended sediment would result in less interactions between PFAS and the RemBind™ surfaces.⁴³ It has also been speculated that this pore blockages have less of an impact on electrostatic interactions when the anion exchange capacity has not been reached, as anion exchange occurs on a molar basis.^{48,49} Additionally, while hydrophobic interactions are less understood, it is well established that that are dependent on surface area.⁵⁰ Hence, minimizing the surface area available by the addition of suspended sediment can have a significant impact on hydrophobic interactions.

Figure 5. Percent removal of PFCAs by RemBind™ from OGIR SW with and without pretreatment.



A full treatment train column experiment using Biochar Basic and RemBind™ was not conducted and is a limitation of the current study. RemBind™ is high in clay content and is thus applied in the field as powder-coated onto rock aggregates with diameters ranging from 1-2".²³ A column would have needed to be 10-20" in diameter and use hundreds of liters of PFAS contaminated water, which was deemed inappropriate for the purposes of this study. In lieu of a column study, there is a need for a pilot-scale testing in the field to evaluate treatment under real storm conditions.

Conclusions

To date, this the first study addressing the treatment of heavy metals and PFAS as co-contaminants in stormwater. After comparing four sorbents with varying sorption mechanisms for the removal of heavy metals and PFAS, a series of sorbents was determined to be necessary for optimal removal of heavy metals and PFAS due to differences in their physiochemical properties. Biochar Basic and RemBind™, the two sorbents that utilized electrostatic interactions in addition to hydrophobic interactions, were selected for the removal of heavy metals and PFAS,

respectively. Matrix effects of stormwater components were crucial in determining sorbent order to maximize contaminant removal. Organic matter reduced the removal of heavy metals by Biochar Basic, but had a more significant impact on PFAS removal by RemBind™. By pre-treating stormwater with Biochar Basic, there was significantly greater removal of 11 out of 21 PFAS by RemBind™, primarily due to the decrease in stormwater suspended solids. Furthermore, future work could serve to add an additional treatment to the beginning of the treatment train to focus on the removal of organic matter. Finally, the difference in sorbent performance in synthetic stormwaters and real stormwaters indicates that synthetic stormwater, even relatively complex in nature, is not a suitable alternative to field-collected stormwater when evaluating sorbents.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Oregon State University in Corvallis, Oregon, is located within the traditional homelands of the Mary's River or Ampinefu Band of Kalapuya. Following the Willamette Valley Treaty of 1855, Kalapuya people were forcibly removed to reservations in Western Oregon. Today, living descendants of these people are a part of the Confederated Tribes of Grand Ronde Community of Oregon (grandronde.org) and the Confederated Tribes of the Siletz Indians (ctsi.nsn.us).

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