Electronic Supplemental Information (ESI)

Evaluation of Sorbents and Matrix Effects for Treating Stormwater Containing Heavy Metals and Per- and Polyfluoroalkyl Substances

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HPLC-TQD-MS Method

Separation and quantification of PFAS were performed using an Agilent 1100 series HPLC (Santa Clara, CA) that was interfaced with a Triple Quadrupole MS/MS system (Waters Corporation Milford, MA). A C_{18} delay column (4.6x 50mm x 5µm Zorbax Eclipse) was fitted between the HPLC pump and autosampler to offset any systemic instrument PFAS contamination. Large volume injection (900 µL) was used for analysis of all samples. Chromatographic separation of all analytes utilized an Eclipse C18 analytical column (4.6x 75mm x 3.5µm). Mobile phases consisted of 20mM ammonium acetate in HPLC grade water (A) and HPLC grade methanol (B). The gradient conditions consisted of 100% mobile phase A at 0.5 mL/min for 3.5 min, switching to 100% mobile phase B at a rate of 1 mL/min for 1.5 min, and then reverting back to mobile phase A at 1.0 mL/min for 4.5 min. After 4.5 min, the flow rate was reduced to 0.5 mL/min for 0.5 min, yielding a total run time of 10 min. The LOQ for this study was defined as the lowest calibration standard (20 ng/L) used in the analysis. No samples contained levels of PFAS above the highest level (10,000 ng/L) of the calibration curve.

Table S1. PFAS Native and Isotopically Labelled Surrogate Standards

Chemical Name	Acronym	Neutral Molecular Formula[1]	Surrogate Standard
Perfluoro-n-butanoic acid	PFBA[2]	C4HO2F7	MPFBA
Perfluoro-n-pentatonic acid	PFPeA	C5HO2F9	M3PFPeA
Perfluoro-n-hexanoic acid	PFHxA	C6HO2F11	M2PFHxA
Perfluoro-n-heptanoic acid	PFHpA	C7HO2F13	M4PFHpA
Perfluoro-n-octanoic acid	PFOA	C8HO2F15	M4PFOA
Perfluoro-n-nonanoic acid	PFNA	C9HO2F17	M5PFNA
Perfluoro-n-decanoic acid	PFDA	C10HO2F19	MPFDA
Perfluoro-n-undecanoic acid	PFUdA	C11HO2F21	MPFUdA
Perfluorobutane sulfonate	PFBS	C4HO3SF9	M3PFBS
Perfluoropentane sulfonate	PFPeS	C5HO3SF11	M3PFBS
Perfluorohexane sulfonate	PFHxS	C6HO3SF13	MPFHxS
Perfluoroheptane sulfonate	PFHpS	C7HO3SF15	MPFOS
Perfluorooctane sulfonate	PFOS	C8HO3SF17	MPFOS
Perfluorononane sulfonate	PFNS	C9HO3SF19	MPFOS
Perfluorodecane sulfonate	PFDS	C10HO3SF21	MPFOS
Perfluorohexane sulfonamide	FHxSA	C6H2O2NSF13	M8FOSA
Perfluorooctane sulfonamide	FOSA	C8H2O2NSF17	M8FOSA
dodecafluoro-3H-4,8-dioxanonanoate	ADONA	C7H2O4F12	MPFDA
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	C8HF16ClSO4	MPFOS
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11Cl-PF3OUdS	C10HF20ClSO4	MPFOS
2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoro propoxy)-propanoic acid	HFPO-DA	C6HF11O3	MHFPO-DA

Table S2. Synthetic and OGSIR Stormwater Composition

	Simple Synthetic	OGSIR SW	Complex Synthetic	Complex Synthetic w/ Iron
NH3-N (mg N/L)	N/A	0.166	0.166	0.166
NO3-N + NO2-N (mg N/L)	N/A	0.051	0.051	0.051
PO4-P (mg P/L)	N/A	0.028	0.028	0.028
Cl (mg/L)	35.4	1.58	9.03	9.03
SO4-S (mg/L)	N/A	2.26	2.25	2.25
F (mg/L)	N/A	0.05	N/A	N/A
Br (mg/L)	N/A	0.02	N/A	N/A
Na (mg/L)	22.9	4.28	6.49	6.49
K (mg/L	N/A	0.91	0.909	0.909
Ca (mg/L)	N/A	9.7	9.7	9.7
Mg (mg/L)	N/A	1.68	1.71	1.71
Fe (ug/L)	N/A	210	N/A	1500
HCO3 (mM)	0.185	N/A	N/A	N/A
DOC (mg C/L)	N/A	11	N/A	N/A

Table S3. OGSIR stormwater composition with and without treatment

	OGSIR Stormwater	Treated OGSIR Stormwater (Treated with Biochar Basic)
pH	7.3	6.7 (little change)
Alkalinity (mg CaCO3/L)	27	8 (moderate removal)
Suspended Sediment (mg/L)	9.3	2.2 (high removal)
Dissolved Solids (mg/L)	94	73 (moderate removal)
DOC (mg C/L)	11	11 (no removal)
Fe (ug/L)	210	27 (high removal)
TDN (mg N/L)	3.8	2.6 (moderate removal)
TDP (mg P/L)	0.32	0.32 (no removal)

Table S4. Average percent removal, 95CI, and percent relative standard deviation (%RSD) of heavy metals and PFAS from screening with synthetic stormwater (n=3 replicates).

	Copper	Zinc	PFOA	PFHxS	PFOS
	Average ± 95CI (% RSD)	Average ± 95CI (% RSD)	Average ± 95CI (% RSD)	Average ± 95CI (% RSD)	Average ± 95CI (% RSD)
Biochar Basic	93 ± 2 (1.8%)	75 ± 45 (53%)	6.5 ± 14.7 (200%)	4.8 ± 14.7 (270%)	1.8 ± 19.2 (940%)
EarthLite	99 ± 0.3 (0.3%)	96 ± 41 (38%)	28 ± 17 (54%)	27 ± 4.4 (16%)	55 ± 20 (33%)
Calgon F400	69 ± 17 (25%)	2.5 ± 4.5 (160%)	28 ± 5 (15%)	81 ± 17 (20%)	64 ± 3 (4.4%)
RemBind	82 ± 3 (2.9%)	60 ± 28 (42%)	95 ± 3 (2.8%)	84 ± 7 (7.6%)	91 ± 4 (4.0%)

Table S5. Percent Removal of PFAS by RemBind™ from OGSIR SW with and without pretreatment (n = 4).

	No Pretreatment (avg ± SD)	With Pretreatment (avg ± SD)
PFBA	22.9 ± 22.1	31.2 ± 11.7
PFPeA	25.0 ± 24.5	30.7 ± 9.4
PFBS	19.9 ± 17.1	25.9 ± 11.3
PFHxA	17.5 ± 22.2	27.3 ± 13.2
PFPeS	30.7 ± 11.3	34.0 ± 12.1
HFPO-DA	34.4 ± 14.7	37.9 ± 22.5
PFHpA	30.5 ± 13.5	33.5 ± 6.4
PFHxS	1.6 ± 12.1	17.7 ± 11.6
ADONA	-1.3 ± 23.1	32.7 ± 18.9
PFOA	15.1 ± 20.5	41.9 ± 17.1
PFHpS	7.2 ± 21.2	34.6 ± 30.7
FHxSA	36.0 ± 12.2	85.6 ± 3.5
PFOS	20.8 ± 10.5	57.1 ± 6.9
PFNA	18.6 ± 17.1	61.8 ± 8.1
9Cl-PF3ONS	26.7 ± 11.8	29.4 ± 9.3
PFNS	54.6 ± 16.5	85.7 ± 1.5
PFDA	20.4 ± 21.4	76.8 ± 6.6
FOSA	74.4 ± 7.2	95.4 ± 0.4
PFDS	38.8 ± 12.7	79.6 ± 2.5
PFUdA	11.7 ± 19.9	78.1 ± 1.2
11Cl-PF3OUdS	66.6 ± 7.6	85.9 ± 2.7