Electronic Supplemental Information for

Controlling Saturation to Improve Per- and Polyfluoroalkyl Substance (PFAS) Removal in Biochar-Amended Stormwater Bioretention System

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Synthetic Stormwater Mixture

Synthetic stormwater mixture was prepared according to Pritchard et al.[1]

Table SI.1 Ingredient list to prepare synthetic stormwater.

Ingredient	Quantity Added	
NWSSB Catch-Basin Material	3	g dry/L
*$CaCl_2$*2H_20*	96	mg/L
*$MgCl_2$*6H_2O*	11	mg/L
$NaHCO_3$	84.01	mg/L
*NaH_2PO_4*H_2O*	2.21	mg/L
$NaNO_3$	6.12	mg/L
Na_2SO_4	43.8	mg/L
NH_4Cl	3.85	mg/L
DOC Concentrate	8	mg C/L

DOC Generation Procedure

DOC straw tea was generated as previously discussed in Pritchard et al.[1] Briefly, 50 g straw (straw wattle; Home Depot) per L DI water was steeped for five days, then filtered using a 200-400 mesh sieve and thoroughly stirred, then filtered through a 47-mm diameter glass microfiber filter (Whatman) in a clean vacuum apparatus, then autoclaved and stored at 4°C.

Influent Concentrations

Table SI.2. Target PFAS compounds analyzed with influent concentrations. Separate values are given for storm 24, which had PFAS spiked in incorrectly.

PFAS	PFAS Class	Concentration [ng/L]	Std. Dev.	Std. Error	Concentration [ng/L] (Storm 24)	Std. Dev. (Storm 24)	Std Error (Storm 24)
PFPeS	*PFSA*	96.4	35.4	6.9	4.9	0.3	0.2
PFHxS	*PFSA*	461.3	161.3	31.6	34.0	0.4	0.2
PFHpS	*PFSA*	64.7	22.0	4.3	9.0	0.1	0.1
PFOS	*PFSA*	3924.6	1283.8	247.1	1360.5	9.4	5.4
PFPeA	*PFCA*	31.4	14.6	3.1	26.0	3.1	1.8
PFHxA	*PFCA*	79.0	26.0	4.9	25.9	0.8	0.4
PFOA	*PFCA*	90.2	32.5	6.1	12.5	0.3	0.2
Cl-PFOS	*Cl-PFSA*	79.4	30.9	5.9	29.3	1.1	0.6
FBSA	*FASA*	5.6	3.1	0.6	7.8	0.2	0.1
FHxSA	*FASA*	83.9	33.5	6.6	57.0	1.6	0.9
PFEtCHxS	*Cyclic PFAS*	19.3	6.5	1.5	2.2	0.3	0.2

Table SI.3. Semiquantitative PFAS compounds analyzed with influent concentrations. Values were not calculated for storm 24 because of inaccuracy in spiking.

PFAS	PFAS Class	Semi-Quantitative Concentration [ng/L]	Std. Dev.	Std. Error
AmPr-FBSA-PrA	*AmPr-FASA-PrA*	125	51	11.7
AmPr-FPeSA-PrA	*AmPr-FASA-PrA*	94	51	11.7
AmPr-FHxSA-PrA	*AmPr-FASA-PrA*	449	179	46.2
AmPr-FBSA	*AmPr-FASA*	25	13	3.0
AmPr-FPeSA	*AmPr-FASA*	15	7	1.6
AmPr-FHxSA	*AmPr-FASA*	199	68	13.4

Table SI.4. Metal compounds analyzed with influent concentrations (including storm 24).

Metal	Concentration (mg/L)	Std. Dev.	Std. Error
Cd	0.173	0.021	0.005
Cu	0.137	0.017	0.004
Ni	0.229	0.020	0.005
Pb	0.037	0.014	0.003
Zn	0.182	0.034	0.008

Table SI.5. Trace organic compounds analyzed with influent concentrations (including storm 24).

Hydrophilic TOrC	Concentration (ug/L)	Std. Dev.	Std. Error
Atrazine	34.05	4.17	0.67
Benzotriazole	22.81	4.12	0.66
Diuron	34.86	4.95	0.79
Fipronil	29.57	9.91	1.59
Imidacloprid	37.62	10.04	1.61
Mecoprop	42.87	8.75	1.40

Table SI.6. List of hydrophobic organic compounds included at 0.1 ug/L.

Hydrophobic TOrC	CAS
Fluorene	86-73-7
Anthracene	120-12-7
Fluoranthene	206-44-0
Pyrene	129-00-0
Benz[a]anthracene	56-55-3
Benzo[a]pyrene	50-32-8
PCB-52	35693-99-3
PCB-77	32598-13-3
PCB-101	37680-73-2
PCB-118	31508-00-6
PCB-126	57465-28-8
Bifenthrin	82657-04-3
Permethrin	52645-53-1
TNT	118-96-7
DNAN	119-27-7
PCB-30	35693-92-6
PCB-204	74472-52-9
PCB-14	34883-41-5
PCB-65	33284-54-7
PCB-166	41411-63-6
naphthalene-d8	1146-65-2
acenaphthene-d10	15067-26-2
anthracene-d10	1719-06-8
pyrene-10	1718-52-1
chrysene-d12	1719-03-5
benzo[a]pyrene-d12	63466-71-7
2-fluorobiphenyl	321-60-8
terphenyl-d14	1718-51-0

LC-MS Analysis Procedure

Samples were injected into a Sciex Exion high-performance liquid chromatography (HPLC-MS) system with a Gemini C18 column (3mm x 100mm, Phenomenex), one SecurityGuard™™C18 Guard Cartridge (4mm x 2mm, Phenomenex) and two Zorbax DIOL guard columns (4.6 mm x 12.5 mm, Agilent). Column oven was set to 40°C. Mobile phase eluents were (A) 20 mM ammonium acetate (Fisher Scientific) in water (Optima™ LC-MS grade) and (B) methanol (Optima™ LC-MS grade). Gradient at 0.6 mL/min was as follows: 0-0.5 min 90% A, 10% B; 0.5-8 min 50% A, 50% B; 8-13 min 1% A, 99% B; 13-20 min 90% A, 10% B). A SCIEX X500R QToF-MS system was used in ESI- mode and collected precursor ion data for m/z 100-1200 Da. Ion spray voltage was set at -4500 V. Temperature was set at 550°C with ion source gas pressure 60 psi, curtain gas pressure 35 psi, CAD gas pressure 10 psi, collision energy -5 V, declustering potential -20 V. Data analyses were performed in Sciex OS software.

Table SI.7. List of suspect compounds included in this study with full names, calibrants for semiquantitation, and PFAS confidence in identification[2] (PCA) levels.

Acronym	Suspect Name	Calibrant	PCI Level
AmPr-FBSA	*N-dimethyl ammonio propyl perfluorobutane sulfonamide*	EtFOSA	2b
AmPr-FPeSA	*C5*	EtFOSA	2b
AmPr-FHxSA	*C6*	EtFOSA	2a
AmPr-FBSA-PrA	*N-dimethyl ammonio propyl perfluorobutane sulfonamido propanoic acid*	EtFOSAA	3a
AmPr-FPeSA-PrA	*C5*	EtFOSAA	3a
AmPr-FHxSA-PrA	*C6*	EtFOSAA	3a

LOQs

Table SI.8. Target compound minimum and maximum limits of quantification for aqueous PFAS samples [ng/L].

	PFPeS	PFHxS	PFOS	PFPeA	PFHxA	PFOA	Cl-PFOS	FHxSA
1 min	2.82	20	20	5	5	10	2	1.95
1 max	2000	10000	10000	10000	5000	2000	200	1000
5 min	0.5	0.5	100	2	5	2	5	2
5 max	500	500	10000	500	5000	500	500	10000
6 min	2.82	20	20	5	5	10	2	1.95
6 max	2000	10000	10000	10000	5000	2000	200	1000
8 min	2.82	20	20	5	5	10	2	1.95
8 max	2000	10000	10000	10000	5000	2000	200	1000
10 min	50	50	50	50	50	50	50	100
10 max	5000	5000	10000	10000	2000	5000	5000	10000
12 min	2.82	20	20	5	5	10	2	1.95
12 max	2000	10000	10000	10000	5000	2000	200	1000
14 min	2.82	20	20	5	5	10	2	1.95
14 max	2000	10000	10000	10000	5000	2000	200	1000
16 min	2.82	20	20	5	5	10	2	1.95
16 max	2000	10000	10000	10000	5000	2000	200	1000
18 min	2.82	20	20	5	5	10	2	1.95
18 max	2000	10000	10000	10000	5000	2000	200	1000
20 min	5	10	66	10	5	10	5	10
20 max	200	1000	10000	1000	1000	10000	200	500
22 min	2.82	20	20	5	5	10	2	1.95
22 max	2000	10000	10000	10000	5000	2000	200	1000
24 min	5	10	66	10	5	10	5	10
24 max	200	1000	10000	1000	1000	10000	200	500

Table SI.9. Target compound minimum and maximum limits of quantification for soil PFAS samples [ng/L].

	PFPeA	PFHxA	PFHpA	PFOA	PFNA	FBSA	FHxSA	MeFOSA	EtFOSA	FOSAA
min	5	20	10	50	20	10	50	50	5	10
max	2000	20000	2000	10000	2000	1000	20000	20000	200	1000

	MeFOSAA	EtFOSAA	PFPrS	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFEtCHxS	Cl-PFOS
min	5	50	50	5	5	100	50	200	5	50
max	1000	1000	20000	2000	2000	20000	20000	20000	200	10000

Table SI.10. Minimum levels of quantification for metals samples.

	Cd	Cu	Ni	Pb	Zn
min	0.0004	0.0013	0.0012	0.0034	0.0005

PFAS Removal Figures Not Shown in Manuscript

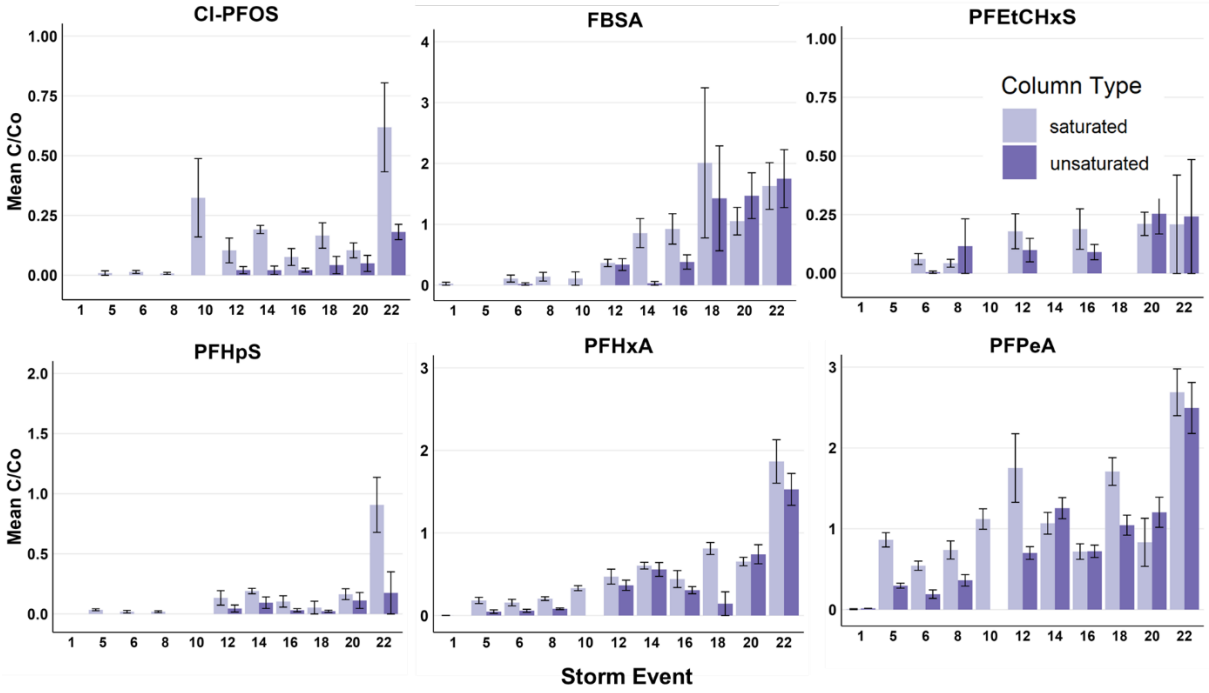

Figure SI.1. Removal of PFAS target compounds not included in primary manuscript.

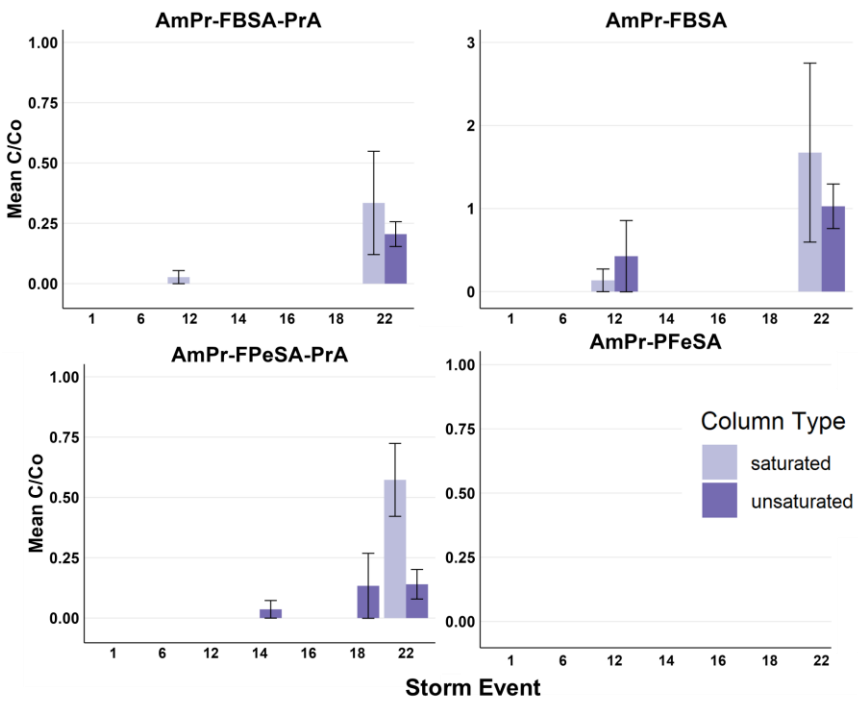

Figure SI.2. Removal of suspect compounds not included in original manuscript.

PFAS Removal (Concentrations)

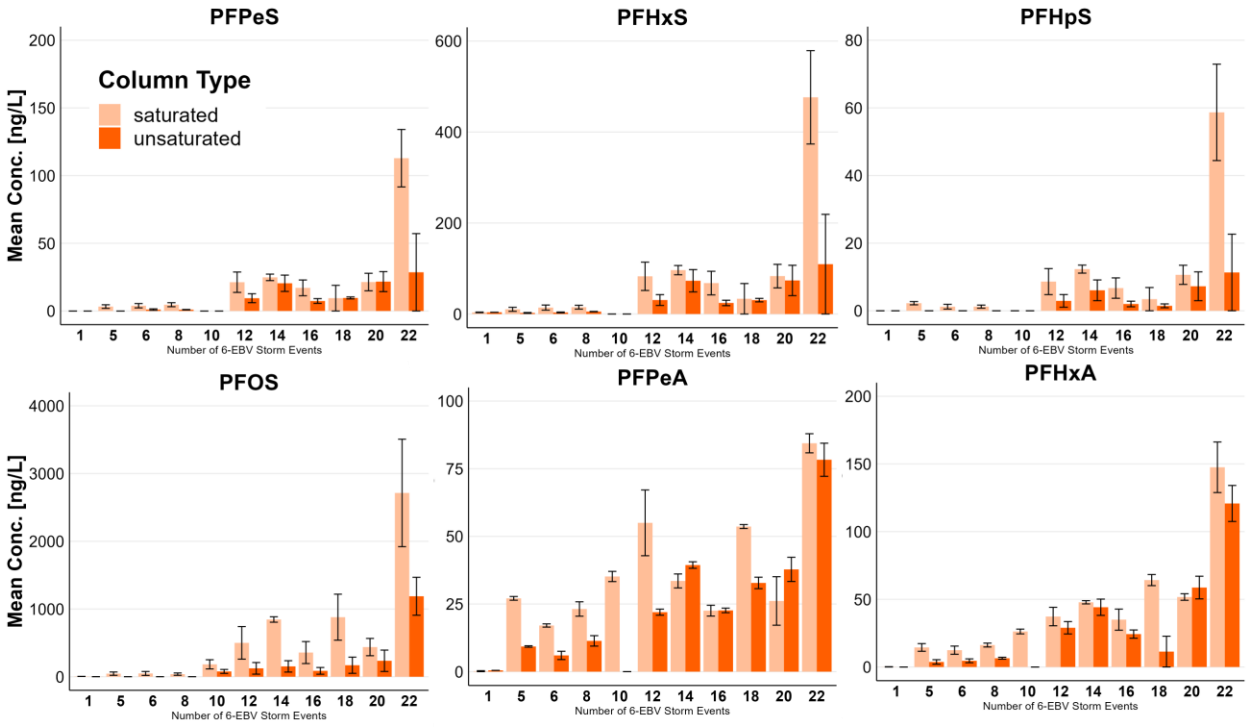

Figure SI.3. PFAS target compound removal in concentrations.

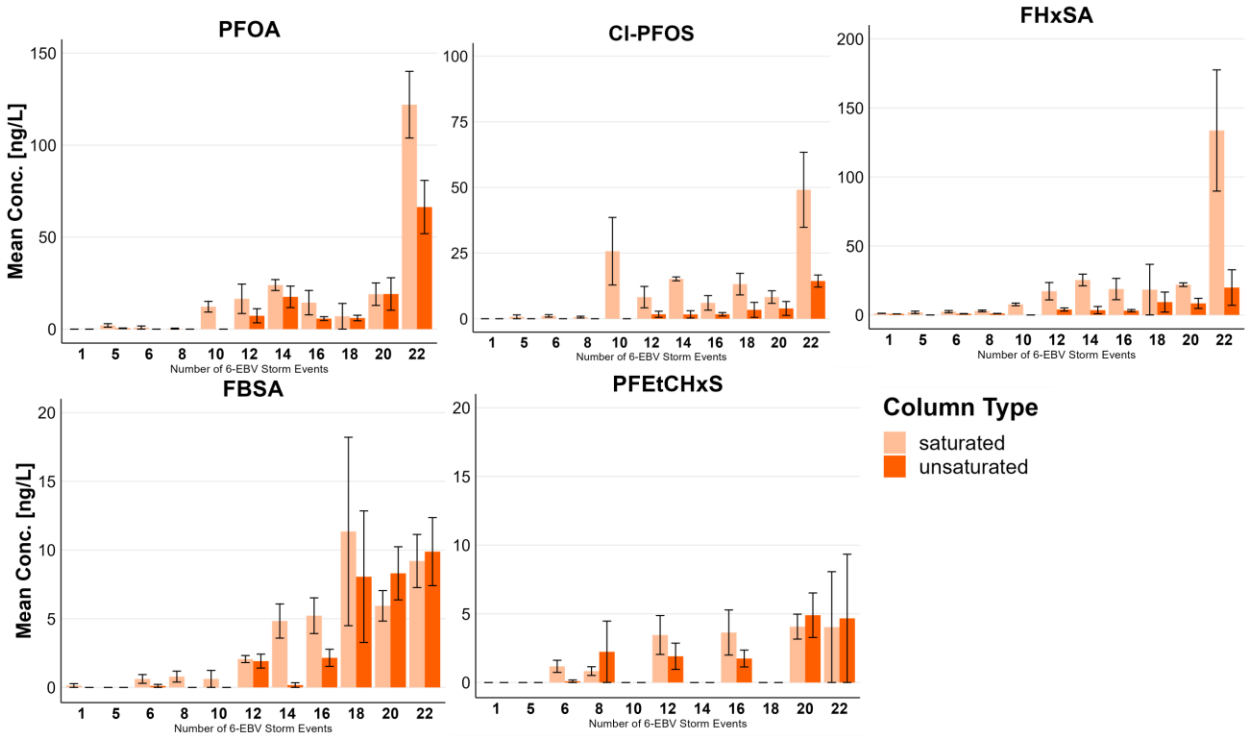

Figure SI.4. PFAS target compound removal in concentrations.

PFAS Removal (Storm 24 Included)

PFAS removal figures with storm event 24 included. Storm 24 had an error with PFAS spiking (see table SI.2 for influent concentrations.)

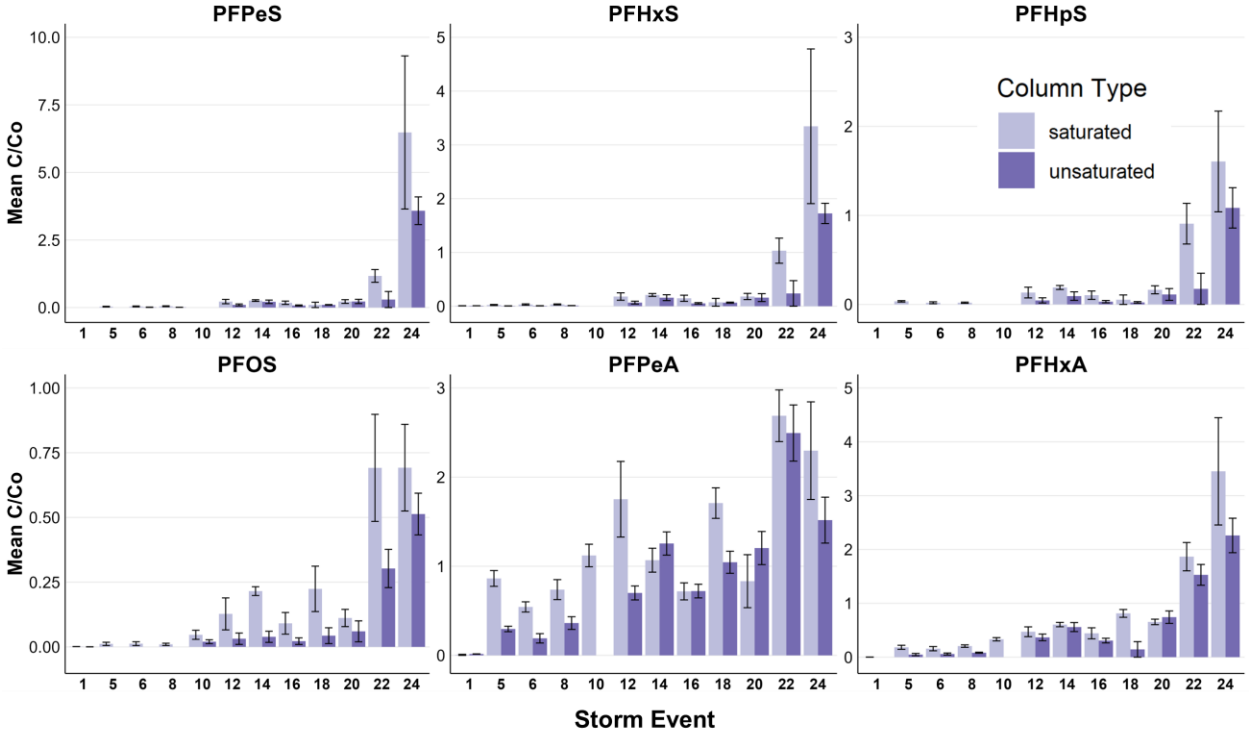

Figure SI.5. Target compound removal with storm 24 included (storm 24 is normalized to its own influent, here.)

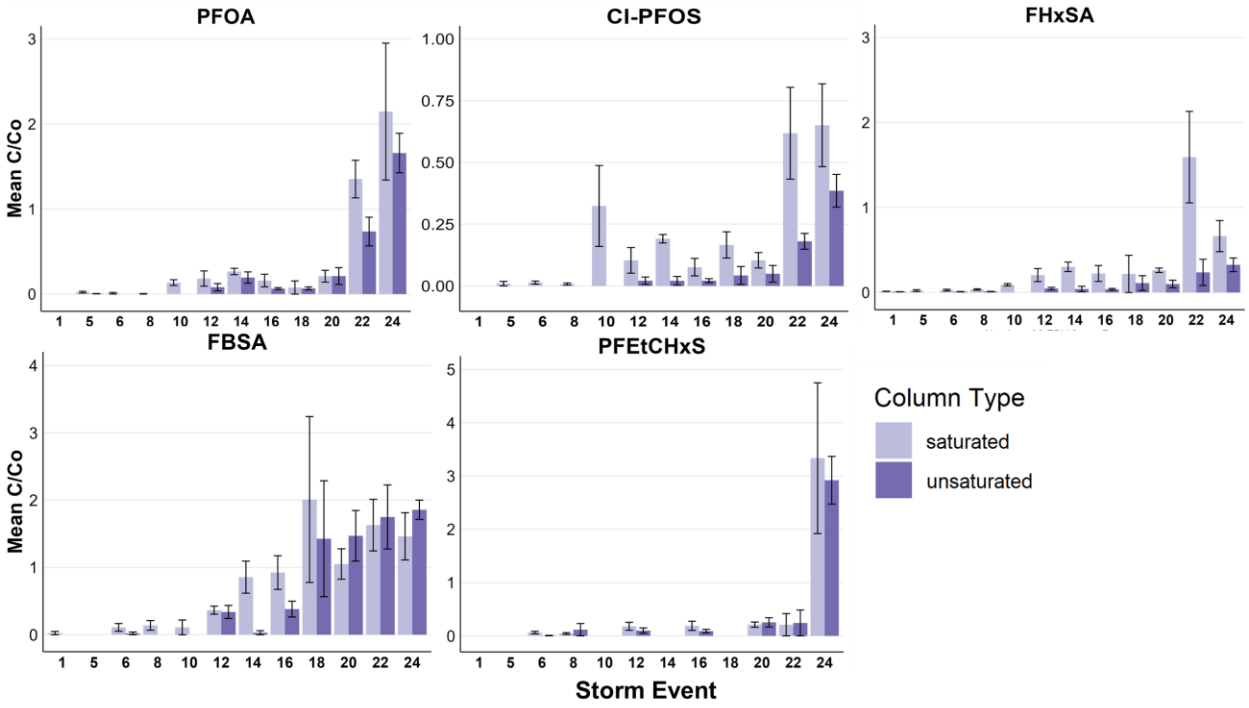

Figure SI.6. Target compound removal with storm 24 included (storm 24 is normalized to its own influent, here.)

Metals Removal

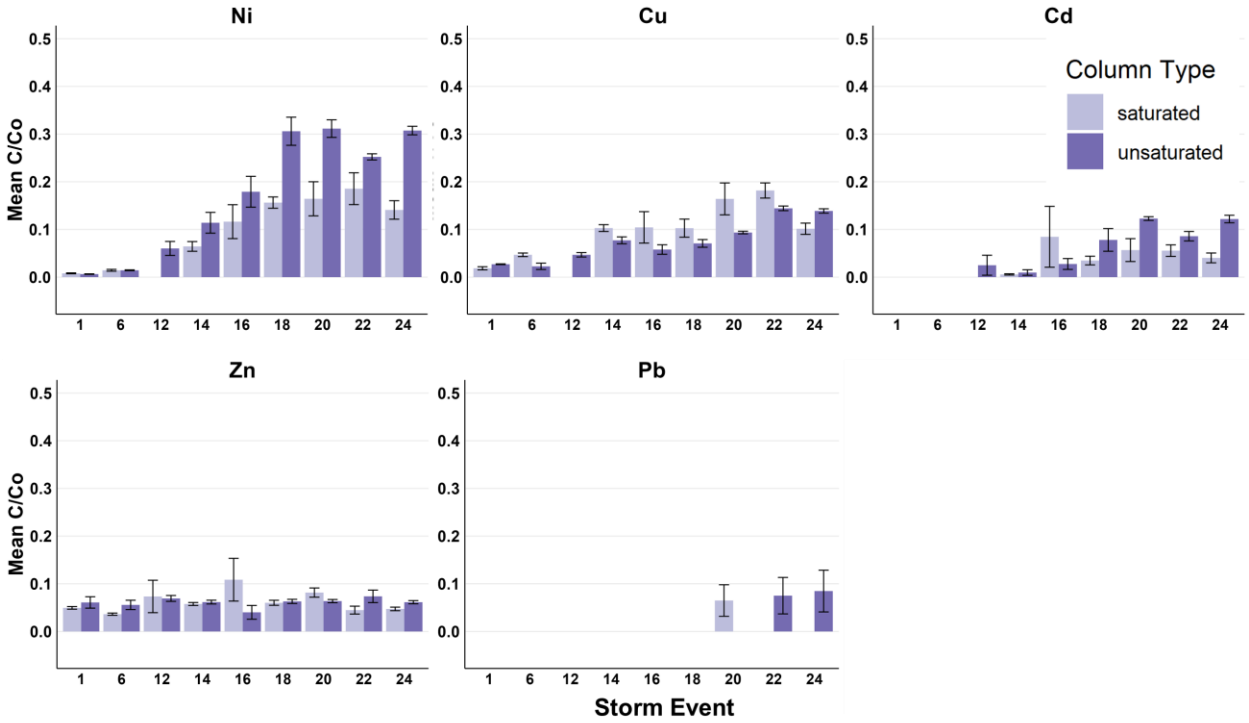

Figure SI.7. Metals removal.

Trace Organics Removal

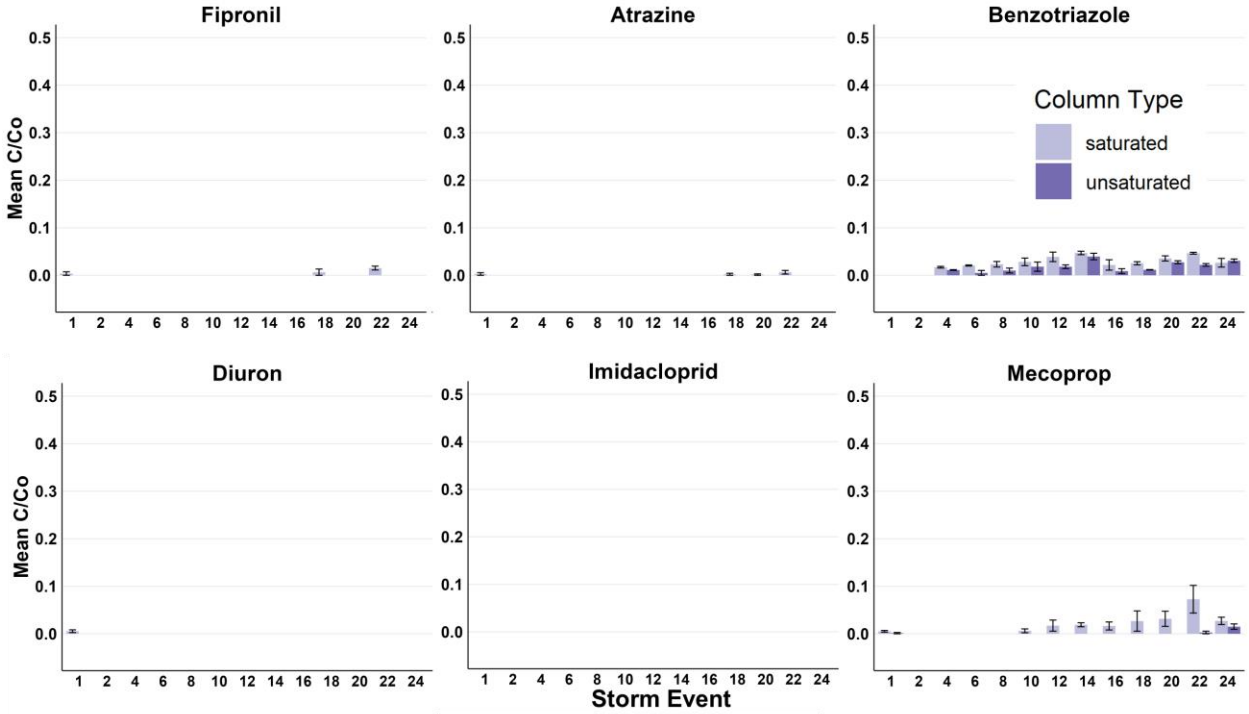

Figure SI.8. Trace organic compounds removal.

Tracer Test

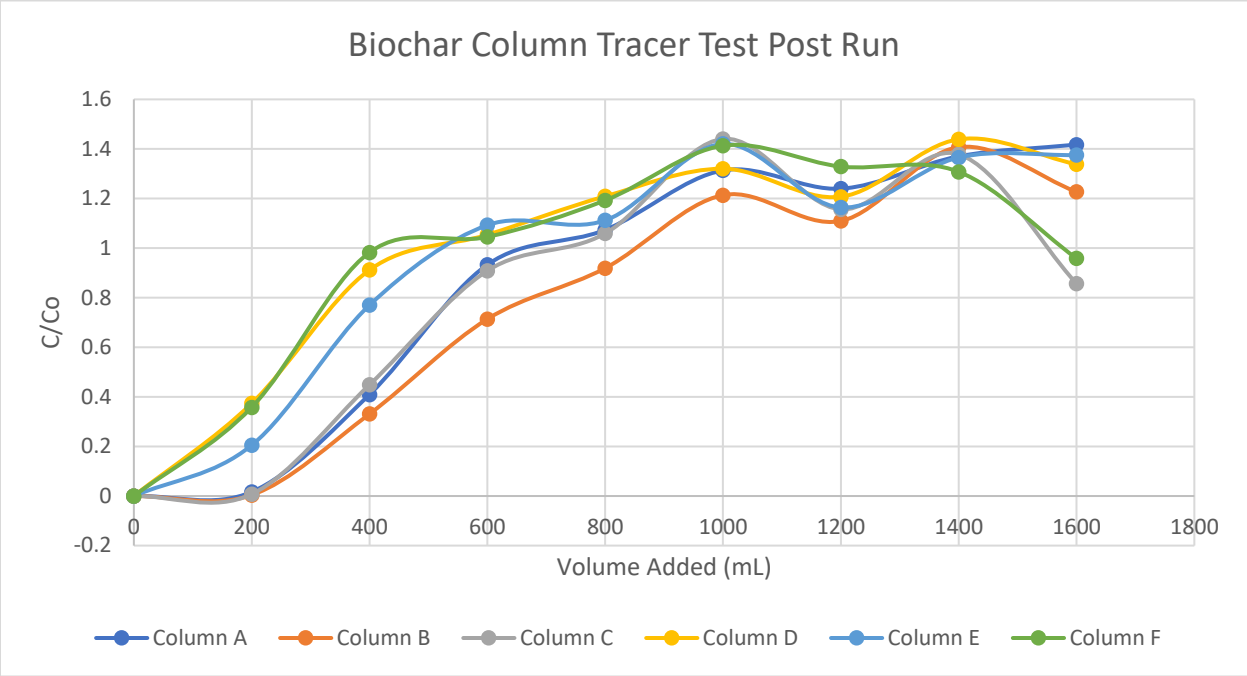

Figure SI.9. Tracer test performed with 240 ppm Br over 1600 mL.

Additional Water Quality Parameters

Table SI.10. Water quality parameters of influent and unsaturated and saturated effluent

	DO (mg/L)	NO_3-N (mg/L)	pH (s.u.)	NH_3-N (mg/L)	PO_4^{3-} (mg/L)	Conductivity (uS)
Influent	5.48 (0.71)	2.46 (3.41)	7.72 (0.27)	1.75 (0.81)	2.85 (1.01)	430 (105)
Saturated effluent	4.45 (0.39)	1.78 (0.29)	7.73 (0.07)	0.49 (0.15)	1.72 (0.28)	450 (37)
Unsaturated effluent	6.08 (0.33)	3.68 (0.55)	7.85 (0.10)	<LOQ	1.58 (0.25)	459 (77)

Flush as Percentage of Retained on Media

Table SI.11. Mass in media, flush load, and flush as percentage of retained PFAS in soil.

Contaminant	Saturation type	Class	Amount in soil [ng]	Flush load [ng]	Flush as percentage of retained in soil
PFPeS	*Saturated*	*PFSA*	5220	63	1.21%
PFPeS	*Unsaturated*	*PFSA*	6150	59	0.96%
PFHxS	*Saturated*	*PFSA*	29900	133	0.44%
PFHxS	*Unsaturated*	*PFSA*	36900	137	0.37%
PFHpS	*Saturated*	*PFSA*	5160	28	0.54%
PFHpS	*Unsaturated*	*PFSA*	6400	26	0.41%
PFOS	*Saturated*	*PFSA*	307000	951	0.31%
PFOS	*Unsaturated*	*PFSA*	456000	1546	0.34%
PFNS	*Saturated*	*PFSA*	420	21	4.95%
PFNS	*Unsaturated*	*PFSA*	630	17	2.69%
PFPeA	*Unsaturated*	*PFCA*	510	135	26.25%
PFPeA	*Saturated*	*PFCA*	500	94	18.88%
PFHxA	*Saturated*	*PFCA*	36700	149	4.06%
PFHxA	*Unsaturated*	*PFCA*	3810	170	4.47%
PFOA	*Saturated*	*PFCA*	5070	47	0.93%
PFOA	*Unsaturated*	*PFCA*	580	47	0.81%
FBSA	*Saturated*	*FASA*	1180	76	6.42%
FBSA	*Unsaturated*	*FASA*	2580	76	2.94%
FHxSA	*Saturated*	*FASA*	8620	120	1.43%
FHxSA	*Unsaturated*	*FASA*	15100	120	0.80%
Cl-PFOS	*Saturated*	*Cl-PFAS*	5610	45	0.80%
Cl-PFOS	*Unsaturated*	*Cl-PFAS*	7690	46	0.60%
PFEtCHxS	*Saturated*	*Cyclic PFAS*	2140	37	1.73%
PFEtCHxS	*Unsaturated*	*Cyclic PFAS*	2430	34	1.40%

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2 J. A. Charbonnet, C. A. McDonough, F. Xiao, T. Schwichtenberg, D. Cao, S. Kaserzon, K. V. Thomas, P. Dewapriya, B. J. Place, E. L. Schymanski, J. A. Field, D. E. Helbling and C. P. Higgins, *Environ. Sci. Technol. Lett.*, 2022, **9**, 473–481.