

## **Supporting Information**

### **Pilot Scale Removal of Per- and Polyfluoroalkyl Substances and Precursors from AFFF-Impacted Groundwater by Granular Activated Carbon**

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## **Introduction**

The pilot-scale GAC demonstration site is a former fire training area (FTA) where airplane fire event simulations were completed from 1958 through 1991. The volume of AFFF applied by fire fighters is unknown. It is likely that both ECF-based and FT-based AFFF were used at the site over the decades of active fire training. Historically, fire training exercises were performed almost weekly, but during the last few years of operation, the site was used only about once a month. These training activities of fire simulation involved fuels and solvents being discharged to a mock steel airplane where they were ignited. Note that it is possible that more recent (>1990s) formulations of AFFF were also added to PFAS contamination in groundwater due to military activities. The site has an on-going full-scale pump and treat system for removing Volatile Organic Compounds (VOCs) and PFOS and PFOA in groundwater. The changeout frequency for the lead GAC vessel, based on 50% breakthrough (exhaustion), was designed to be approximately 250 days or every 7-8 months. Since operation of the full-scale GAC system, the treated effluent is discharged to a series of six lateral infiltration galleries. The changeout of the carbon has been more frequent than it was designed. The frequent changeout has resulted in higher operation and maintenance costs for this pump and treat system, which shows the need to fully understand the factors that accelerate GAC loading and lead to spent GAC. Due to the mixed uses of ECF and FT AFFF at the site, precursors are abundant, in-situ transformation have also occurred due to implementation of remediation technologies, such as soil vapor extraction, air sparging, and in-situ chemical oxidation, aerobic or anaerobic biodegradation. Currently, groundwater remediation at this site includes air sparging to remediate VOCs and a pump and treat system for VOCs and PFOA and PFOS.

## **Experimental**

**Solvents and Chemicals-** For analysis HPLC grade water (>99%, high purity, Burdick and Jackson brand), hydrochloric acid (BDH Chemicals), and ammonium acetate (reagent grade, Macrom Chemicals) were purchased from VWR (Radnor, PA). Sodium hydroxide (98%, reagent grade), ethyl acetate (99.9%, reagent grade), potassium persulfate (>99%, ACS reagent), and 2,2,2-Trifluoroethanol (99%, Fluka Analytical) were purchased from Sigma Aldrich (St. Louis, MO). Methanol (>99%, LC/MS grade) was purchased from Fisher Scientific (Hampton, NH).

## Individual PFASs by LC-MS/MS

**Table S1. LC-MS/MS target analyte full name, acronym, acquisition masses and parameters, internal standard, calibration reference, and data quality.**

Analyte	Acronym	PI* (m/z )	CV * (V)	FI- 1* (m/z )	CE* (eV )	FI- 2* (m/z )	CE* (eV )	Internal Standard	Calibration Reference	Data Quality *	LO Q (ng/L)
Perfluorobutanoic acid	PFBA	213	20	169	8	n/a	n/a	[ <sup>13</sup> C <sub>4</sub> ]PFBA	PFBA	Qn	10
Perfluoropentanoic acid	PFPeA	263	20	219	8	n/a	n/a	[ <sup>13</sup> C <sub>3</sub> ]PFPeA	PFPeA	Qn	10
Perfluorohexanoic acid	PFHxA	313	20	269	8	119	22	[ <sup>13</sup> C <sub>2</sub> ]PFHxA	PFHxA	Qn	10
Perfluoroheptanoic acid	PFHpA	363	20	319	8	169	14	[ <sup>13</sup> C <sub>4</sub> ]PFOA	PFHpA	Sq	10
Perfluorooctanoic acid	PFOA	413	20	369	8	169	18	[ <sup>13</sup> C <sub>4</sub> ]PFOA	PFOA	Qn	10
Perfluorononaic acid	PFNA	463	22	429	8	169	18	[ <sup>13</sup> C <sub>5</sub> ]PFNA	PFNA	Qn	10
Perfluorodecanoic acid	PFDA	513	22	469	10	269	18	[ <sup>13</sup> C <sub>2</sub> ]PFDA	PFDA	Qn	10
Perfluoroundecanoic acid	PFUnDA	563	22	519	10	169	22	[ <sup>13</sup> C <sub>2</sub> ]PFUnD A	PFUnDA	Qn	10
Perfluorododecanoic acid	PFDoDA	613	22	569	10	169	24	[ <sup>13</sup> C <sub>2</sub> ]PFDoD A	PFDoDA	Qn	10
Perfluorotridecanoic acid	PFTriDA	663	24	619	12	169	26	[ <sup>13</sup> C <sub>2</sub> ]PFDoD A	PFTriDA	Sq	10
Perfluorotetradecanoic acid	PFTeDA	713	24	669	12	169	26	[ <sup>13</sup> C <sub>2</sub> ]PFDoD A	PFTeDA	Sq	10
N-sulfo propyl perfluorobutane sulfonamide	SPr-FBSA	420	40	78	22	298	28	[ <sup>13</sup> C <sub>4</sub> ]PFOA	PFOA	Ql	10
N-sulfo propyl perfluoropentane sulfonamide	SPr-FPeSA	470	40	78	22	348	28	[ <sup>13</sup> C <sub>4</sub> ]PFOA	PFOA	Ql	10
N-sulfo propyl perfluorohexane sulfonamide	SPr-FHxSA	520	40	78	30	398	30	[ <sup>13</sup> C <sub>4</sub> ]PFOA	PFOA	Ql	10

Perfluoropropane sulfonate	PFPrS	249	46	80	32	99	26	[ <sup>18</sup> O <sub>2</sub> ]PFBS	PFPrS	Ql	10
Perfluorobutane sulfonate	PFBS	299	50	80	32	99	26	[ <sup>18</sup> O <sub>2</sub> ]PFBS	PFBS	Qn	10
Perfluoropentane sulfonate	PFPeS	349	56	80	34	99	28	[ <sup>18</sup> O <sub>2</sub> ]PFHxS	PFHxS	Sq	10
Branched Perfluorohexane sulfonate	Br-PFHxS	399	58	80	36	99	28	[ <sup>18</sup> O <sub>2</sub> ]PFHxS	PFHxS	Qn	10
Perfluorheptane sulfonate	PFHpS	449	64	80	46	99	32	[ <sup>13</sup> C <sub>2</sub> ]PFOS	PFOS	Sq	10
Branched Perfluorooctanesulfonic acid	Br-PFOS	499	70	80	46	99	34	[ <sup>13</sup> C <sub>2</sub> ]PFOS	PFOS	Qn	10
Perfluorononane sulfonate	PFNS	549	72	80	50	99	36	[ <sup>13</sup> C <sub>2</sub> ]PFOS	PFDS	Sq	10
Perfluorodecane sulfonate	PFDS	599	76	80	52	99	36	[ <sup>13</sup> C <sub>2</sub> ]PFOS	PFDS	Sq	10
4:2 fluorotelomer sulfonate	4:2 FTS	327	42	307	19	81	26	[ <sup>13</sup> C <sub>2</sub> ] 4:2 FtS	4:2 FTS	Qn	10
6:2 fluorotelomer sulfonate	6:2 FTS	427	40	407	22	81	28	[ <sup>13</sup> C <sub>2</sub> ] 6:2 FtS	6:2 FTS	Qn	10
8:2 fluorotelomer sulfonate	8:2 FTS	527	45	507	25	81	32	[ <sup>13</sup> C <sub>2</sub> ] PFDA	8:2 FTS	Qn	10
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-aminium	6:2 FtSaB	571	78	104	28	58	38	M-PFOS	6:2 FtSaB	Sq	10
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-aminium	6:2 FtSaAm	513	60	58	44	86	34	M-PFOS	PFOS	Sq	10
Perfluoropropane sulfonamide	FPrSA	248	40	78	32	119	26	M-PFBS	PFBS	Ql	10

Perfluorobutane sulfonamide	FBSA	298	50	119	26	78	32	M-PFBS	PFBS	QI	10
Perfluoropentane sulfonamide	FPeSA	348	40	78	35	119	35	M-FOSA	FOSA	QI	10
Perfluorohexane sulfonamide	FHxSA	398	58	78	36	119	28	M-FOSA	FHxSA	Qn	50
Perfluorooctane sulfonamide	FOSA	498	40	78	30	319	30	M-FOSA	FOSA	Qn	50
Perfluorobutane sulfinate	PFBSi	283	50	83	32	119	26	M-PFBS	PFBS	QI	10
Perfluoropentane sulfinate	PFPeSi	333	40	83	35	119	35	M-PFPeA	PFPeA	QI	10
Perfluorohexane sulfinate	PFHxSi	383	20	319	40	83	40	M-PFHxA	PFHxA	QI	10
Perfluorooctane sulfinate	PFOSi	483	40	119	40	419	40	M-PFOA	PFOA	QI	10
6:2 fluorotelomer sulfonyl propanoamido-dimethylethyl sulfonate	6:2 FTSO2PrAd-DiMeEtS	618	40	203	30	152	30	M-PFOA	PFOA	QI	10
8:2 fluorotelomer sulfonyl propanoamido-dimethylethyl sulfonate	8:2 FTSO2PrAd-DiMeEtS	718	40	206	30	152	30	M-PFOA	PFOA	QI	10
N-sulfo propyl dimethyl ammonio propyl perfluorobutane sulfonamide	SPrAmPr-FBSA	507	40	383	40	182	40	M-FOSA	FOSA	QI	10
N-sulfo propyl dimethyl ammonio propyl perfluoropentane sulfonamide	SPrAmPr-FPeSA	557	40	433	40	182	40	M-FOSA	FOSA	QI	10
N-sulfo propyl dimethyl ammonio propyl perfluorohexane sulfonamide	SPrAmPr-FHxSA	607	40	483	40	182	40	M-FOSA	FOSA	QI	10
N-Trimethylammoniopropyl perfluorobutane	TAmPr-FBSA	399	40	60	40	116	40	M-FOSA	FOSA	QI	10

sulfonamide												
N-Trimethylammoniopropyl perfluoropentane sulfonamide	TAmPr-FPeSA	449	40	60	40	116	40	M-FOSA	FOSA	QI	10	
N-Trimethylammoniopropyl perfluorohexane sulfonamide	TAmPr-FHxSA	499	40	60	40	116	40	M-FOSA	FOSA	QI	10	
6:2 fluorotelomer thia propanoamido dimethyl ethyl sulfonate	6:2 FTTh-PrAd-DiMeEtS	586	35	135	20	80	20	M-PFOS	PFOS	QI	10	
N-methylperfluorooctane sulfonamido acetic acid	N-MeFOSAA	570	34	169	20	419	10	M-N-MeFOSAA	N-MeFOSA A	Qn	10	
N-ethylperfluorooctane sulfonamido acetic acid	N-EtFOSAA	584	34	419	20	526	20	M-N-EtFOSAA	N-EtFOSAA	Qn	10	
3-Perfluoropentyl propanoic acid (5:3)	FPePA	341	19	237	14	217	24	M-PFPeA	PFPeA	Sq	10	
2H-perfluoro-2-octenoic acid	FHUEA	357	18	293	17	243	34	M-PFHxA	PFHxA	Sq	10	
2-perfluorohexylethanoic acid	FHEA	377	20	293	22	63	7	M-PFHxA	PFHxA	Sq	10	
Perfluorooctane sulfonamido acetic acid	FOSAA	556	45	498	27	78	40	M-PFOA	PFOA	Sq	10	
Perfluoro[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]butanoic acid	[ <sup>13</sup> C <sub>4</sub> ] PFBA	217	20	172	8	n/a	n/a	n/a	n/a	n/a	n/a	
Perfluoro[3,4,5- <sup>13</sup> C <sub>3</sub> ]pentanoic acid	[ <sup>13</sup> C <sub>3</sub> ] PFPeA	266	20	222	8	n/a	n/a	n/a	n/a	n/a	n/a	
Perfluoro[1,2- <sup>13</sup> C <sub>2</sub> ]hexanoic acid	[ <sup>13</sup> C <sub>2</sub> ] PFHxA	315	20	270	8	n/a	n/a	n/a	n/a	n/a	n/a	
Perfluoro[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]heptanoic acid	[ <sup>13</sup> C <sub>4</sub> ] PFHpA	367	15	322	11	n/a	n/a	n/a	n/a	n/a	n/a	

Perfluoro[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octanoic acid	[ <sup>13</sup> C <sub>4</sub> ] PFOA	417	20	372	8	n/a	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2- <sup>13</sup> C <sub>2</sub> ]octanoic acid	[ <sup>13</sup> C <sub>2</sub> ] PFOA	415	20	370	9	n/a	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4,5- <sup>13</sup> C <sub>5</sub> ]nonanoic acid	[ <sup>13</sup> C <sub>5</sub> ] PFNA	468	22	423	8	n/a	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2- <sup>13</sup> C <sub>2</sub> ]decanoic acid	[ <sup>13</sup> C <sub>2</sub> ] PFDA	515	22	470	10	n/a	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2- <sup>13</sup> C <sub>2</sub> ]undecanoic acid	[ <sup>13</sup> C <sub>2</sub> ] PFUnDA	565	22	519	10	n/a	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2- <sup>13</sup> C <sub>2</sub> ]dodecanoic acid	[ <sup>13</sup> C <sub>2</sub> ] PFDoDA	615	22	570	10	n/a	n/a	n/a	n/a	n/a	n/a
2H-Perfluoro-[1,2- <sup>13</sup> C <sub>2</sub> ]-2-octenoic acid	[ <sup>13</sup> C <sub>2</sub> ] FHUEA	359	18	294	17	n/a	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-[2,3,4- <sup>13</sup> C <sub>3</sub> ]-butanesulfonate	[ <sup>13</sup> C <sub>2</sub> ] PFBS	302	31	99	30	n/a	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-hexane[ <sup>18</sup> O <sub>2</sub> ]sulfonate	[ <sup>18</sup> O <sub>2</sub> ] PFHxS	403	58	103	28	n/a	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octane sulfonate	[ <sup>13</sup> C <sub>2</sub> ] PFOS	503	70	99	34	n/a	n/a	n/a	n/a	n/a	n/a
4:2[1,2- <sup>13</sup> C <sub>2</sub> ] fluorotelomer sulfonate	[ <sup>13</sup> C <sub>2</sub> ] 4:2 FTS	329	30	81	25	n/a	n/a	n/a	n/a	n/a	n/a
6:2 [1,2- <sup>13</sup> C <sub>2</sub> ] fluorotelomer sulfonate	[ <sup>13</sup> C <sub>2</sub> ] 6:2 FTS	429	44	409	22	n/a	n/a	n/a	n/a	n/a	n/a
8:2 [1,2- <sup>13</sup> C <sub>2</sub> ] fluorotelomer sulfonate	[ <sup>13</sup> C <sub>2</sub> ] 8:2 FTS	529	45	81	35	n/a	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-[ <sup>13</sup> C <sub>8</sub> ]octane sulfonamide	[ <sup>13</sup> C <sub>8</sub> ] FOSA	506	40	78	30	n/a	n/a	n/a	n/a	n/a	n/a
Methyl-d <sub>3</sub> -perfluorooctane sulfonamido acetic acid	[ <sup>2</sup> H <sub>3</sub> ] MeFOSAA	573	34	419	20	n/a	n/a	n/a	n/a	n/a	n/a
Ethyl-d <sub>5</sub> -perfluorooctane sulfonamido acetic acid	[ <sup>2</sup> H <sub>5</sub> ] EtFOSAA	589	34	419	20	n/a	n/a	n/a	n/a	n/a	n/a

\*PI (precursor ion), CV (cone voltage), FI (fragmentation ion), CE (collision energy), Qn (quantitative), Sq (semiquantitative), Ql (qualitative), Sc (Screen)[1-3]



**Analysis by LC-QTOF.** Analysis for all individual PFASs were performed on a Shimadzu Exion HPLC (Shimadzu, Kyoto, Japan) attached to a Sciex X500R quadrupole time of flight mass spectrometer (Sciex, Concord, Canada). All instrumental conditions and parameters can be found in Barzen-Hanson et al., 2017.[3] It is important to note that analysis was performed in suspect screening mode for approximately 300 individual PFASs. Non-target analysis for additional unknown PFASs was outside of the scope of this study. In an attempt to identify the PFAS mass in the influent, an upgradient groundwater sample nearer to the source zone than the influent sample in this study was analyzed by LC-QTOF as part of a prior experiment in Barzen-Hanson et al..[3] LC-QTOF analysis identified 52 individual PFASs, and all 52 observed PFASs are included in the LC-MS/MS method created for this study. However, when the positively validated LC-MS/MS method was used to screen the influent, only 16 PFASs were routinely observed.

**TOP Assay-** Equation S2 assumes equal molar conversion of known precursors to PFCAs after oxidation. No attempt was made to account for expected molar concentrations of any individual precursor due to variability of precursor recovery of TOP assay in the authors' previous work and between other laboratories.[4, 5]

TOP assay calculations:

Table S2. Influent analyte concentrations before and after TOP assay (ng/L and nmol)  $\pm$  standard error and summed masses (nmol)  $\pm$  propagated standard error.

	Analyte	MW	Before TOP Assay (ng/L)	After TOP Assay (ng/L)	Before TOP Assay (nmol)	After TOP Assay (nmol)	Net production (nmol)
Known PFCAs	PFBA	214	78 $\pm$ 14	510 $\pm$ 37	0.36 $\pm$ 0.18	2.4 $\pm$ 0.1	2.0 $\pm$ 0.1
	PFPeA	264	400 $\pm$ 83	970 $\pm$ 110	1.5 $\pm$ 0.1	3.7 $\pm$ 0.2	2.2 $\pm$ 0.2
	PFHxA	314	690 $\pm$ 140	5300 $\pm$ 460	2.2 $\pm$ 0.2	17 $\pm$ 1	15 $\pm$ 1
	PFHpA	364	150 $\pm$ 19	230 $\pm$ 16	0.41 $\pm$ 0.02	0.63 $\pm$ 0.02	0.22 $\pm$ 0.03
	PFOA	414	900 $\pm$ 210	1200 $\pm$ 390	2.2 $\pm$ 0.2	2.9 $\pm$ 0.4	0.70 $\pm$ 0.50***
	PFNA	464	23 $\pm$ 16	88 $\pm$ 7	0.050 $\pm$ 0.015	0.19 $\pm$ 0.05	0.14 $\pm$ 0.05***
Known PFSA	PFBS	300	16 $\pm$ 3	<10	0.053 $\pm$ 0.005	<0.040	***
	PFPeS	350	28 $\pm$ 9	<10	0.080 $\pm$ 0.011	<0.033	***
	PFHxS	400	1600 $\pm$ 430	1400 $\pm$ 190	4.0 $\pm$ 0.5	3.5 $\pm$ 0.2	***
	PFHpS	450	87 $\pm$ 34	65 $\pm$ 17	0.19 $\pm$ 0.03	0.14 $\pm$ 0.02	***
	PFOS	500	3500 $\pm$ 470	2900 $\pm$ 220	7.0 $\pm$ 0.4	5.8 $\pm$ 0.2	***
Known Precursors	4:2 FtSA	328	12 $\pm$ 3	<3.3	0.037 $\pm$ 0.009	<0.030	
	6:2 FtSA	428	1100 $\pm$ 130	<3.3	2.6 $\pm$ 0.1	<0.023	
	8:2 FtSA	528	180 $\pm$ 68	<3.3	0.34 $\pm$ 0.06	<0.19	
	FPeSA	348	82 $\pm$ 36	<3.3	0.24 $\pm$ 0.05	<0.14	
	FHxSA	398	2500 $\pm$ 380	<17	6.3 $\pm$ 0.4	<0.13	
	FOSA	448	360 $\pm$ 86	<17	0.80 $\pm$ 0.09	<0.11	
	N-Tamp-FHxSA	499	91 $\pm$ 29	<3.3	0.18 $\pm$ 0.05	<0.020	
Summary	$\Sigma$ PFCAs (nmol)				6.7 $\pm$ 0.8	27 $\pm$ 1	20 $\pm$ 2
	$\Sigma$ PFSA (nmol)				11 $\pm$ 1	9.4 $\pm$ 0.3	***
	$\Sigma$ Known precursors (nmol)				10 $\pm$ 0	<LOD	
	$\Sigma$ Total PFASs (nmol)				27.7 $\pm$ 1	36.4 $\pm$ 1	

\*\*\*The difference in the mean values of the two groups is not great enough to reject the possibility that the difference is due to random sampling variability. Sampling variability is defined as >30%. There is not a statistically significant difference between the TOP assay before and after oxidation.

a) Calculation for net production of PFCAs:

$$\begin{aligned} \text{Net Production of PFCAs (nmol)} \\ = \Sigma((PFBA_{\text{after oxid}} - PFBA_{\text{before oxid}}) + (PFPeA_{\text{after oxid}} - PFPeA_{\text{before oxid}}) + (PFHxA_{\text{after oxid}} \\ - PFHxA_{\text{before oxid}}) + (PFHpA_{\text{after oxid}} - PFHpA_{\text{before oxid}}) + (PFOA_{\text{after oxid}} - PFOA_{\text{before oxid}}) + (PFNA_{\text{after oxid}} \\ - PFNA_{\text{before oxid}})) \end{aligned}$$

Example:  $\text{Net Production of PFCAs (nmol)} = \Sigma((2.4 - 0.36) + (3.7 - 1.5) + (17 - 2.2) + (0.63 - 0.41) + (2.9 - 2.2) + (0.19 - 0.050)) = 20.10 \text{ nmol}$

b) Calculation for net production of PFCAs (simplified):

$$\text{Net Production of PFCAs (nmol)} = \Sigma PFCAs_{\text{after oxid}} - \Sigma PFCAs_{\text{before oxidation}}$$

Example:  $\text{Net Production of PFCAs (nmol)} = 27 - 6.7 = 20 \text{ nmol}$

c) **Equation S1.** Calculation of unknown precursor mass.

$$\text{Unknown Precursor Mass (nmol)} = \Sigma PFCAs_{\text{after oxid}} - \Sigma PFCAs_{\text{before oxid}} - \Sigma \text{Known Precursors}_{\text{before oxid}}$$

Example:  $\text{Unknown Precursor Mass (nmol)} = 27 - 6.7 - 10 = 9.6 \text{ nmol}$

d) **Equation S2.** Calculation of total mass of PFASs accounted for before the TOP assay (%).<sup>ψ</sup>

Total mass accounted for by known PFAS (%)

$$= \left( \frac{(\Sigma PFCAs_{\text{before oxid}} + \Sigma PFASs_{\text{before oxid}} + \Sigma \text{Known Precursors}_{\text{before oxid}})}{(\Sigma PFCAs_{\text{after oxid}} + \Sigma PFASs_{\text{after oxidation}})} \times 100 \right)$$

Example:  $\text{Total mass accounted for by known PFAS (\%)} = \left( \frac{(6.7 + 11 + 10)}{(27 + 9.4)} \times 100 \right) = \left( \frac{27.7}{36.4} \times 100 \right) = 76\%$

‡As a result of the insignificant, but different, values for  $\Sigma$ PFASs before and after oxidation the authors' have elected to underestimate the total mass accounted for by known PFAS (%) by using  $\Sigma$ PFASs before oxidation.

## Results and Discussion:

### Breakthrough curves

Figure S1. Breakthrough curves for PFCAs, PFSAs, 6:2 FtS, and FHxSA in lead vessel effluent. Red stars denote the  $C/C_0$  for the TOP assay at select bed volumes.

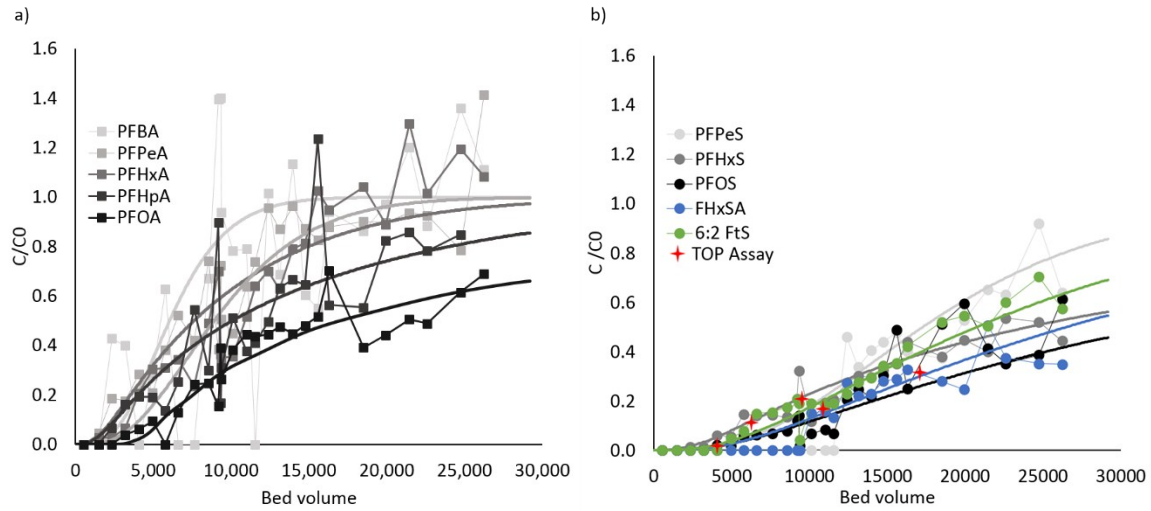
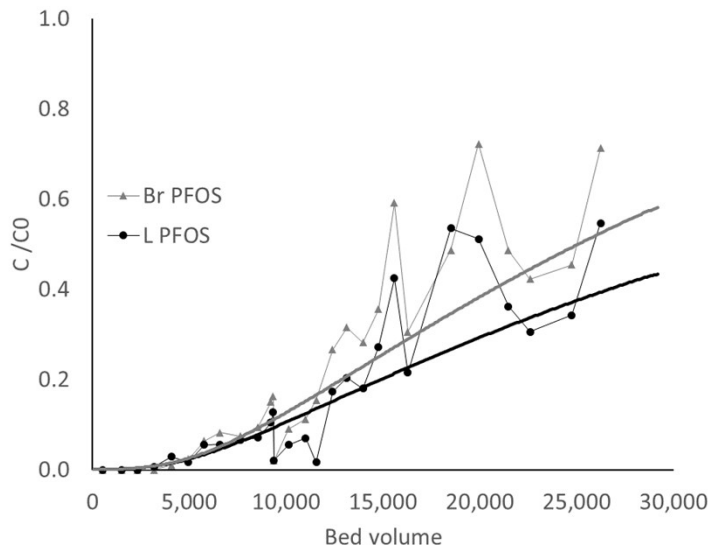


Figure S2. Breakthrough curves for Br- and L-PFOS in lag vessel effluent.



## References

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