Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supplemental Information

Non-Targeted Identification and Semi-Quantitation of Emerging Per- and Polyfluoroalkyl Substances (PFAS) in US Rainwater

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Table S1. PFAS Class Acronyms

Acronym	Definition
FTCAs	Fluorotelomer carboxylic acids
FTOHs	Fluorotelomer alcohols
FTUCAs	Fluorotelomer unsaturated carboxylic acids
H-PFCAs	H-substituted perfluorocarboxylic acids (single F atom to H atom substitution)
H-PFdiCAs	H-substituted perfluoro dicarboxylic acids
oPFSAs	Odd perfluoroalkyl sulfonic acids (alternating CH_2 and CF_2 groups in the alkyl chain)
PFCAs	Perfluorocarboxylic acids
PFECAs	Perfluoroalkyl ether carboxylic acids
PFECAs+	Perfluoroalkyl ether carboxylic acids, unsaturated PFECAs, H-substituted PFECAs, and H-substituted unsaturated PFECAs
PFSAs	Perfluoroalkyl sulfonic acids

Table S2. Number of samples and blanks

Site	Number of Samples	Number of Blanks
Ashland, OH	7	2 site blanks
Rockford, OH	8	2 site blanks[(a)]
Shaker Heights, OH	10	0
Whitestown, IN	5	2 site blanks + 1 ride-along blank
Willoughby, OH	10	1 site blank
Wooster, OH	10	0[(b)]
Jackson Hole, WY	3	0[(b)]

[(a)] One of the site blanks was extracted in duplicate.
[(b)] Site blanks for Wooster and Jackson Hole were analyzed in Pike et al.[1] for targeted measurements by liquid chromatography triple quadrupole mass spectrometry, but insufficient sample volume remained for nontargeted measurements by liquid chromatography quadrupole time-of-flight mass spectrometry.

Table S3. HPLC-QTOF Instrument Parameters

HPLC Parameters

Solvent		
Solvent A	water, 10 mM ammonium acetate	
Solvent B	methanol, 10 mM ammonium acetate	
Flow rate	0.250 mL/min	
Temp	50°C	
Solvent Program	A	B
0.00 min	60%	40%
3.00 min	60%	40%
12.00 min	35%	65%
22.00 min	0%	100%
27.00 min	0%	100%
Post time	5 min	
Inj. volume	7 μL (with needle wash)	

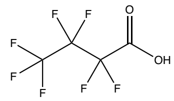
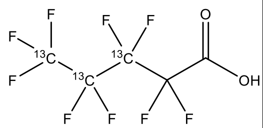
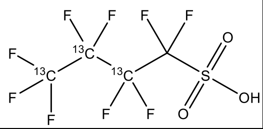
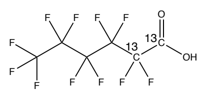
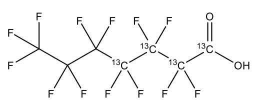
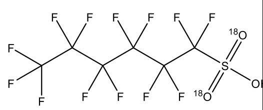
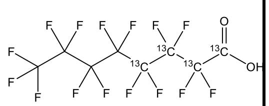
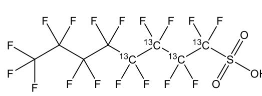
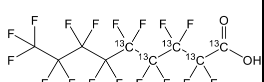
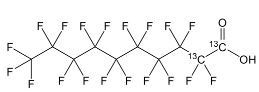
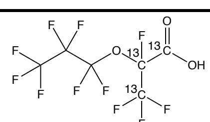
QTOF Parameters

Mode	Negative ion
Needle voltage	-4,000 V
Nozzle voltage	500 V
Fragmentor	125 V
Skimmer	65 V
Scan Range	100-1,100 m/z
Ref Mass	Yes, 112.9856, 1033.9881
MS/MS	Auto with Preferred ions
Collision energy	40 V
Isolation width	4 amu (medium)
Scan range	70-1,700 m/z
Scan rate	1 spectrum/sec

Table S4. MS-DIAL v4.60 Parameters

Centroid Parameters	
MS1 tolerance	0.02
MS2 tolerance	0.025
Isotope Recognition	
Maximum charged number	2
Peak Detection Parameters	
Smoothing	Linear weighted moving average
Level	3
Minimum peak width	5
Minimum peak height	5000
Peak Spotting Parameters	
Mass slice width	0.1
MSP and MS/MS Identification Settings	
MSP file	FluoroMatch 2.0 Library
Accurate mass tolerance (MS1)	0.02
Accurate mass tolerance (MS2)	0.05
Identification score cut-off	80
Text File and Post Identification (Retention Time and Accurate Mass Based)	
Text file	In-house database
Retention time tolerance	0.1
Accurate mass tolerance	0.02
Identification score cut-off	85
Adducts	
$[M-H]^-$	Yes
$[M+Hac-H]^-$	Yes
Alignment Parameters	
Reference file	Pooled sample
Retention time tolerance	0.1
MS1 tolerance	0.025
Retention time factor	0.5
MS1 factor	0.5
Peak count filter	0
N% detected in at least 1 group	0
Remove feature based on peak height fold-change	TRUE
Sample max / blank average	5
Sample average / blank average	5
Keep identified and annotated metabolites	TRUE
Keep removable features and assign tag for checking	TRUE
Gap filling by compulsion	TRUE

Table S5. Mass labelled standards detected by HPLC-QTOF and number of detections per 93 samples

Compound	Structure	Formula	RT (min)	Ref *m/z*	*m/z*	Δppm	Detects
PFBA[a]		$C_4HF_7O_2$	5.99	212.9787	212.9799	3.52	91/93
[M3]PFPeA		$[^{13}C]_3C_2HF_9O_2$	9.62	265.9861	265.9865	1.50	90/93
[M3]PFBS		$[^{13}C]_3CHF_9O_3S$	9.88	301.9531	301.9535	1.32	90/93
[M2]PFHxA		$[^{13}C]_2C_4HF_{11}O_2$	11.11	314.9795	314.9793	-0.57	90/93
[M4]PFHpA		$[^{13}C]_4C_3HF_{13}O_2$	12.59	366.9830	366.9835	1.42	90/93
[M]PFHxS		$C_6HF_{13}O[^{18}O]_2S$	12.60	402.9500	402.9458	10.52	88/93
[M4]PFOA		$[^{13}C]_4C_4HF_{15}O_2$	14.00	416.9788	416.9803	3.57	89/93
[M4]PFOS		$[^{13}C]_4C_4HF_{17}O_3S$	15.27	502.9436	502.9442	-1.15	90/93
[M5]PFNA		$[^{13}C]_5C_4HF_{17}O_2$	15.33	467.9800	467.9808	1.75	90/93
[M]PFDA		$[^{13}C]_2C_8HF_{19}O_2$	16.58	514.9667	514.9679	2.39	91/93
[M3]HFPO-DA[b]		$[^{13}C]_3C_3HF_{11}O_3$	11.55	284.9773	-	-	-

[a] The mass labeled MPFBA surrogate in samples was below the limit-of-detection of the instrument.
[b] [M3]HFPO-DA has the same *m/z* ion as the unlabeled analyte and cannot be isolated.

Table S6. SPE Recoveries

PFAS	Average % Recovery[a] (n = 5)	Standard Error
PFBA	94.4	11.2
PFPeA	86.8	6.1
PFHxA	106.4	4.7
PFHpA	87.6	2.8
PFOA	94.3	2.9
PFNA	93.7	6.1
PFDA	114.9	8.5
PFBS	100.1	8.1
PFHxS	89.2	5.2
PFOS	77.0	6.7

[a] Data were measured by Pike et al.[1] with liquid chromatography triple quadrupole mass spectrometry.

Table S7. PFAS Concentrations in Blanks from Pike et al. (2021)

	Mean Concentration in Blanks (ng L^{-1}) [a]							
PFAS	Method Blanks	Ride-Along	Willoughby OH	Wooster OH	Ashland OH	Rockford OH	Whitestown IN	Jackson Hole
TFA	0.7	2	10	0.9	10	40	20	20
PFBA	0.2	0.2	2	0.1	2	5	30	0.9
PFPeA	0.05	<0.03	0.6	0.003	0.9	1	6	0.5
PFHxA	0.09	0.07	2	0.07	2	3	7	0.2
PFHpA	0.1	0.07	1	0.1	0.5	0.8	2	0.2
PFOA	0.1	0.1	2	1	1	1	2	0.5
PFNA	0.08	0.1	3	0.08	2	1	2	0.1
PFDA	0.1	0.08	5	0.1	1	1	1	0.2
PFOS	1	0.8	10	10	7	10	30	0.7
HFPO-DA	0.03	0.04	0.05	0.02	0.2	0.09	1	0.0004

[a] Data were measured by Pike et al.[1] with liquid chromatography triple quadrupole mass spectrometry.

Table S8. Retention time and peak area variance of PFAS standards (linear isomers, n = 5)

Analyte	CAS #	Retention Time (min)	% RSD Peak Area
Carboxylates			
Perfluoropropionic acid (PFPrA)	422-64-0	3.62 ± 0.05	-
Perfluorobutanoic acid (PFBA)*	375-22-4	6.05 ± 0.05	17.3
Perfluoropentanoic acid (PFPeA)*	2706-90-3	9.64 ± 0.02	13.0
Perflurohexanoic acid (PFHxA)*	307-24-4	11.21 ± 0.03	10.6
Perfluoroheptanoic acid (PFHpA)*	375-85-9	12.64 ± 0.05	4.8
Perfluorooctanoic acid (PFOA)*	335-67-1	14.06 ± 0.07	6.7
Perfluorononanoic acid (PFNA)*	375-95-1	15.42 ± 0.07	6.7
Perfluorodecanoic acid (PFDA)*	335-76-2	16.67 ± 0.08	5.4
Perfluoroundecanoic acid (PFUdA)	2058-94-8	17.85 ± 0.08	5.6
Perfluorododecanoic acid (PFDoA)	307-55-1	18.97 ± 0.08	5.7
Sulfonates			
Perfluorobutanesulfonic acid (PFBS)*	375-73-5	9.86 ± 0.05	10.4
Perfluorohexanesulfonic acid (PFHxS)*	355-46-4	12.65 ± 0.05	6.2
Perfluorooctanesulfonic acid (PFOS)*	1763-23-1	15.34 ± 0.05	6.4
Telomer acids			
2-Perfluorohexyl ethanoic acid (6:2 FTCA)	53826-12-3	13.71 ± 0.07	-
2-Perfluorooctyl ethanoic acid (8:2 FTCA)	27854-31-5	16.00 ± 0.01	-
2-Perfluorohdecyl ethanoic acid (10:2 FTCA)	53826-13-4	18.48 ± 0.01	-
Telomer sulfonates			
1H,1H,2H,2H-perfluorohexane sulfonic acid (4:2 FTS)	757124-72-4	11.05 ± 0.05	23.7
1H,1H,2H,2H-perfluorooctane sulfonic acid (6:2 FTS)	27619-97-2	13.94 ± 0.07	10.2
1H,1H,2H,2H-perfluorodecane sulfonic acid (8:2 FTS)	39108-34-4	16.57 ± 0.07	3.7
Other			
Hexafluoropropylene oxide dimer acid (HPFO-DA)*	13252-13-6	11.58 ± 0.07	-
Perfluorooctanesulfonamide (FOSA)	754-91-6	17.36 ± 0.07	5.5

*Isotopically labelled surrogate added to sample prior to extraction

Table S9. Retention time and peak area variance of PFAS standards in the pooled sample and calibration standard

Surrogate	**Retention Time (min)**	**% RSD Peak Area[a]**
MPFBA[b]	6.01 ± 0.02	9.9
[M3]PFPeA	9.63 ± 0.02	9.6
[M2]PFHxA	11.16 ± 0.04	11.5
[M4]PFHpA	12.58 ± 0.05	8.5
[M4]PFOA	13.99 ± 0.03	10.2
[M5]PFNA	15.31 ± 0.07	7.4
[M]PFDA	16.55 ± 0.07	7.3
[M]PFUdA[b]	17.72 ± 0.07	5.8
[M]PFDoA[b]	18.81 ± 0.08	4.1
[M3]PFBS	9.88 ± 0.03	26
[M]PFHxS	12.58 ± 0.05	6.7
[M4]PFOS	15.24 ± 0.07	5.1
[M3]HFPO-DA	11.56 ± 0.03	-

[a] standard deviation (*n* = 4)

[b] measured using calibration standard

Table S10. Additional emerging PFAS identified in precipitation by QTOF MS/MS

Ret Time (min)	Mass	Formula	Ion	Identity	Level
3.11	371.9851	$C_8H_3F_{11}O_4$	$[M-H]^-$	H-substituted perfluoroalkyl dioic acid	**5a**
4.00	195.9963	$C_4H_2F_6O_2$	$[M-H]^-$	2,3,3,4,4,4-hexafluorobutanoic acid	**3c**
7.36	291.9802	$C_6HF_9O_3$	$[M-H]^-$	unsaturated perfluorocarboxylic acid ether	**3c**
7.77	245.9927	C5H6F8O2	[M-H]-	H-substituted perfluoroalkyl acid	**5a**
7.95	287.9844	$C_7HF_9O_2$	$[M-H]^-$	unsaturated perfluorocarboxylic acid	**5a**
9.56	527.9690	$C_{10}H_5F_{17}O_3S$	$[M-H]^-$		**5a**
9.57	263.9849	$C_5HF_9O_2$	$[M-H]^-$	branched perfluorocarboxylic acid	**3c**
9.66	437.9947	$C_{10}H_4F_{14}O_3$	$[M-H]^-$		**4**
9.78	238.0041	$C_6H_4F_6O_3$	$[M-H]^-$		**4**
10.23	603.0474	$C_{15}H_{18}F_{13}NO_5S_2$	$[M-H]^-$	fluorotelomer sulfinyl amido sulfonic acid	**3c**
10.35	257.9919	$C_6H_2F_8O_2$	$[M-H]^-$	H-substituted perfluorocarboxylic acid	**5a**
10.42	295.9903	$C_6H_2F_{10}O_2$	$[M-H]^-$	H-substituted perfluorocarboxylic acid	**3c**
10.99	287.9990	$C_7H_4F_8O_3$	$[M-H]^-$	H-substituted perfluorocarboxylic acid	**3c**
11.12	313.9825	$C_6HF_{11}O_2$	$[M-H]^-$	2,2,3,4,4,5,5,5-octafluoro-3-(trifluoromethyl)pentanoic acid	**3c**
11.32	307.9906	$C_7H_2F_{10}O_2$	$[M-H]^-$	H-substituted perfluorocarboxylic acid	**3c**
11.68	504.0219	$C_{10}H_{19}F_6N_2O_8PS_2$	$[M-H]^-$		**4**
11.93	972.1595	$C_{12}H_{21}F_7N_2O_6S_2$	$[M-2H]^{2-}$	perfluoroalkyl sulfonamide + amine	**5a**
12.54	753.9617	$C_{18}H_5F_{23}O_4S$	$[M-H]^-$		**4**
13.47	449.9410	$C_7HF_{15}O_3S$	$[M-H]^-$	branched perfluoroalkyl sulfonic acid	**5a**
13.80	438.0087	$C_{10}H_7F_{13}O_2S$	$[M-H]^-$	6:2:1 Fluorotelomer thioether acetic acid	**5a**
14.19	407.9823	$C_9H_2F_{14}$O2	$[M-H]^-$	H-substituted perfluorocarboxylic acid	**5a**
15.19	581.9426	$C_{10}H_2F_{20}O_3S$	$[M-H]^-$	H-substituted perfluoroalkyl sulfonic acid	**3c**
16.73	595.9703	$C_{12}H_2F_{22}O_2$	$[M-H]^-$	H-substituted perfluorocarboxylic acid	**3c**

Table S11. Minimum, maximum, and median PFAS concentrations (ng L^{-1}) at each collection site

Compound	Ashland	Jackson Hole	Rockford	Shaker Heights	Whitestown	Willoughby	Wooster
1	0.27 – 3.9 (1.1) [(a)]	[(b)]	0.36 – 1.4 (0.60)	0.23 – 4.9 (1.3)	0.29 – 1.4 (0.93)	0.002 – 0.80 (0.53)	3.0 – 145 (12)
2	0.28 – 4.5 (1.8)		0.44 – 1.7 (1.1)	0.32 – 9.4 (2.7)	0.54 – 2.1 (1.4)	0.002 – 1.7 (1.1)	14 – 597 (61)
3	0.06 – 1.4 (0.32)	2.1 – 7.0 (5.4)	0.04 – 0.61 (0.17)	0.02 – 1.1 (0.09)	0.02 – 0.39 (0.18)	0.005 – 0.12 (0.06)	27 – 1.25×10^3 (163)
4			n.d.[(c)] – 2.1 (0.40)	0.009 – 3.4 (0.67)	0.001 – 1.1 (0.85)	n.d. – 4.3 (0.43)	n.d. – 53 (6.7)
5	0.02 – 0.57 (0.19)		0.02 – 0.51 (0.09)		0.02 – 0.42 (0.23)	0.04 – 0.17 (0.07)	0.02 – 0.64 (0.27)
6							11 – 139 (41)
7				n.d. – 0.01 (n.d.)			0.78 – 17 (5.4)
8	n.d. – 0.23 (0.15)			0.003 – 1.6 (0.13)			14 – 172 (66)
9	0.004 – 0.16 (0.04)		n.d. – 0.08 (0.02)	n.d. – 0.41 (0.01)			5.1 – 147 (35)
10							19 – 246 (92)
11	n.d. – 3.3 (1.3)		0.81 – 4.1 (2.0)		0.30 – 2.0 (1.5)	n.d. – 1.4 (0.99)	294 – 1.15×10^3 (452)
12							15 – 180. (63)
13			0.90 – 2.4 (1.7)				240 – 2.71×10^3 (922)
14	0.83 – 6.5 (5.5)		0.53 – 4.3 (0.93)	0.32 – 11 (3.0)		0.67 – 4.0 (1.3)	129 – 636 (218)
15	n.d. – 0.59 (0.20)		n.d. – 1.3 (0.48)	n.d. – 2.4 (0.28)		n.d. – 0.78 (0.06)	17 – 72 (31)
16	0.25 – 2.13 (0.47)			0.78 – 5.3 (2.1)			0.24 – 7.3 (4.8)

Compound	Ashland	Jackson Hole	Rockford	Shaker Heights	Whitestown	Willoughby	Wooster
17			0.03 – 0.43 (0.05)	0.02 – 0.77 (0.19)			149 – 2.01×10^3 (687)
18	0.96 – 3.0 (2.1)		0.57 – 4.8 (1.2)	0.37 – 11 (2.9)	0.16 – 3.6 (1.6)	0.10 – 1.8 (0.96)	86 – 1.77×10^3 (414)
19			0.03 – 0.39 (0.12)	0.01 – 0.41 (0.08)			87 – 1.57×10^3 (459)
20	0.47 – 2.0 (0.68)	0.10 – 0.30 (0.21)		0.20 – 7.3 (1.6)	0.12 – 2.0 (1.3)	0.21 – 2.5 (1.3)	28 – 592 (139)
21	0.07 – 0.40 (0.13)			0.02 – 1.2 (0.11)			34 – 889 (218)
23	0.04 – 0.64 (0.14)			0.05 – 2.7 (0.57)			14 – 475 (88)
Σ FTCAs[d]	2.1 – 6.5 (3.9)	2.2 – 7.1 (5.5)	2.4 – 8.7 (5.0)	0.60 – 9.7 (3.1)	1.2 – 3.8 (2.4)	0.04 – 2.3 (1.3)	982 – 1.02×10^4 (3.07×10^3)
Σ FTUCAs	n.d. – 0.59 (0.20)		n.d. – 3.4 (0.58)	0.01 – 3.7 (1.4)	n.d. – 1.1 (0.85)	n.d. – 4.3 (0.49)	21 – 89 (47)
Σ H-PFCAs	3.4 – 11 (7.8)	0.10 – 0.30 (0.21)	1.5 – 5.8 (3.1)	1.4 – 22 (7.3)	0.27 – 5.0 (2.9)	0.15 – 6.8 (3.5)	288 – 3.09×10^3 (782)
Σ H-PFdiCAs	n.d. – 0.23 (0.15)			n.d. – 1.6 (0.13)			25 – 311 (108)
Σ PFCAs	63 – 1.14×10^3 (219)	272 – 874 (313)	79 – 760. (121)	51 – 1.21×10^3 (339)	6.0 – 179 (77)	73 – 176 (96)	151 – 2.29×10^3 (448)
Σ PFECAs+	0.28 – 1.6 (0.98)	0.42 – 2.7 (5.2)	n.d – 2.7 (0.85)	0.16 – 5.1 (1.3)	0.23 – 3.1 (1.5)	0.24 – 2.9 (0.56)	20. – 263 97)
Σ PFSAs	1.1 – 12 (2.3)	0.44 – 48 (5.2)	0.25 – 9.6 (0.77)	3.1 – 13 (6.6)	0.47 – 3.5 (0.78)	4.4 – 11 (8.5)	1.4 – 19 (15)
Σ EPA-Monitored[e]	4.1 – 24 (7.7)	4.7 – 78 (35)	2.8 – 17 (5.9)	4.6 – 48 (18)	1.1 – 12 (7.4)	7.4 – 31 (13)	41 – 608 (115)
Σ Emerging	68 – 1.13×10^3 (231)	270. – 854 (292)	85 – 759 (130.)	51 – 1.23×10^3 (343)	7.6 – 181 (82)	76 – 176 (94)	1.47×10^3 – 1.58×10^4 (4.38×10^3)

Compound	Ashland	Jackson Hole	Rockford	Shaker Heights	Whitestown	Willoughby	Wooster
Σ PFAS	72 – 1.16×10^3 (239)	275 – 932 (327)	88 – 776 (135)	57 – 1.26×10^3 (358)	8.7 – 192 (89)	83 – 191 (113)	1.52×10^3 – 1.64×10^4 (4.45×10^3)

[(a)] The value in parentheses is the median.

[(b)] No values are reported in the empty cells for the compounds at a particular site where the sample concentration was not significantly different from the method blank according to a one-tailed *t*-test ($p < 0.05$). Compounds 22 and 24 from Table 1 were not quantified at any site because of high presence in blanks.

[(c)] n.d. = non-detect

[(d)] The class sums include eight FTCAs, two FTUCAs, four H-PFCAs, two H-PFdiCAs, nine PFCAs, three PFSAs, and three PFECAs+ (one PFECA, one unsaturated PFECA, and one H-substituted unsaturated PFECA).

[(e)] The EPA-monitored group includes ten PFAS: PFHpS (from this work) and the C4-C10 PFCAs, PFOS, and HFPO-DA (from Pike et al.[1]). Each of these compounds appears in EPA Method 533 and/or 537.1.[2,3] We refer to the remaining 22 PFAS, which are not found in the EPA drinking water methods, as emerging PFAS. The emerging group includes compounds **1-15**, **17-21**, and **23** from **Table 1** of this work, along with TFA (trifluoroacetic acid) from Pike et al.[1]

Table S12. Minimum, maximum, and median deposition fluxes (ng m^{-2}) at each collection site

Compound	Ashland	Jackson Hole	Rockford	Shaker Heights	Whitestown	Willoughby	Wooster
1	5.3 – 75 (28)		0.9 – 16 (7.2)	4.2 – 180. (8.7)	1.2 – 24 (1.4)	0.03 – 24 (5.5)	28 – 6.0×10^3 (88)
2	7.0 – 84 (32)		1.1 – 23 (9.1)	6.8 – 345 (14)	1.4 – 36 (2.3)	0.04 – 53 (8.9)	143 – 2.5×10^4 (431)
3	0.5 – 35 (2.8)	14 – 78 (40.)	0.1 – 7.3 (1.6)	0.33 – 42 (1.2)	0.09 – 6.8 (0.5)	0.1 – 2.4 (0.8)	256 – 5.2×10^4 (1.2×10^3)
4			n.d. – 23 (4.2)	0.07 – 34 (11)	n.d. – 24 (3.7)	n.d. – 122 (4.6)	n.d. – 297 (105)
5	0.2 – 7.8 (3.8)		0.12 – 5.5 (0.9)		0.03 – 4.9 (0.9)	0.2 – 5.9 (1.1)	0.09 – 15 (1.8)
6							42 – 5.7×10^3 (372)
7				n.d. – 0.29 (0.02)			7.3 – 681 (51)
8	n.d. – 6.8 (1.1)			0.07 – 12 (1.7)			52 – 7.1×10^3 (466)
9	0.03 – 4.1 (1.1)		n.d. – 1.0 (0.1)	n.d. – 15 (0.03)			20. – 6.1×10^3 (356)
10							90. – 1.0×10^4 (804)
11	n.d. – 64 (39)		2.7 – 44 (23)		0.5 – 39 (3.9)	n.d. – 30. (7.8)	1.2×10^3 – 4.7×10^4 (4.6×10^3)
12							141 – 4.0×10^3 (471)
13			3.6 – 28 (16)				916 – 1.1×10^5 (9.1×10^3)
14	7.0 – 219 (60.)		1.9 – 52 (11)	4.3 – 394 (36)		5.3 – 114 (17)	552 – 2.6×10^4 (2.1×10^3)
15	n.d. – 12 (2.6)		n.d. – 16 (1.4)	n.d. – 7.9 (3.0)		n.d. – 20. (0.3)	65 – 3.0×10^3 (284)
16	2.1 – 43 (12)			8.9 – 194 (23)			0.9 - 144 (54)
17			0.1 – 5.1 (0.6)	0.32 – 10. (2.7)			569 – 8.3×10^4 (5.5×10^3)

Compound	Ashland	Jackson Hole	Rockford	Shaker Heights	Whitestown	Willoughby	Wooster
18	18 – 91 (21)		3.0 – 52 (13)	3.7 – 218 (26)	0.2 – 45 (4.7)	2.0 – 30. (17)	328 – 7.3×10^4 (4.1×10^3)
19			0.1 – 4.4 (0.7)	0.17 – 3.8 (1.0)			330. – 6.5×10^4 (4.4×10^3)
20	3.9 – 78 (14)	0.8 – 2.3 (1.8)		4.3 – 95 (12)	0.2 – 35 (5.3)	7.5 – 36 (20.)	106 – 2.4×10^4 (1.3×10^3)
21	0.5 – 6.3 (2.6)			0.24 – 33 (1.4)			140. – 3.7×10^4 (2.1×10^3)
23	0.7 – 8.1 (1.7)			1.1 – 89 (4.2)			64 – 2.0×10^4 (838)
Σ FTCAs	17 – 156 (59)	14 – 79 (41)	7.8 – 104 (53)	10. – 353 (24)	2.2 – 66 (5.3)	0.6 – 48 (14)	5.0×10^3 – 4.2×10^5 (2.8×10^4)
Σ FTUCAs	n.d. – 12 (2.6)		0.03 – 37 (5.3)	0.24 – 34 (13)	n.d. – 24 (3.7)	n.d. – 122 (6.5)	97 – 3.0×10^3 (404)
Σ H-PFCAs	29 – 376 (116)	0.8 – 2.3 (1.8)	5.0 – 67 (32)	24 – 707 (80.)	0.4 – 80. (9.9)	2.5 – 174 (48)	1.5×10^3 – 1.3×10^5 (4.3×10^4)
Σ H-PFdiCAs	n.d. – 6.8 (1.1)			0.07 – 12 (1.7)			94 – 1.3×10^4 (838)
Σ PFCAs	1.4×10^3 – 1.8×10^4 (7.2×10^3)	795 – 9.8×10^3 (5.2×10^3)	294 – 8.7×10^3 (1.3×10^3)	520. – 3.2×10^4 (3.2×10^3)	9.2 – 2.7×10^3 (253)	393 – 3.9×10^3 (1.8×10^3)	1.2×10^3 – 9.4×10^4 (3.4×10^3)
Σ PFECAs+	1.9 – 63 (9.5)	6.9 – 26 (8.0)	n.d. – 30. (9.5)	3.4 – 58 (13)	0.4 – 56 (4.1)	1.0 – 82 (9.2)	139 – 1.1×10^4 (851)
Σ PFSAs	8.8 – 238 (54)	8.3 – 540. (13)	2.6 – 32 (5.5)	21 – 464 (75)	0.7 – 76 (2.0)	36 – 305 (129)	7.6 – 612 (142)
Σ EPA-Monitored	40. – 488 (173)	89 – 874 (89)	17 – 196 (51)	59 – 1.8×10^3 (186)	1.6 – 264 (14)	65 – 846 (193)	317 – 2.5×10^4 (833)
Σ Emerging	1.5×10^3 – 1.8×10^4 (7.3×10^3)	741 – 9.5×10^3 (5.1×10^3)	287 – 8.7×10^3 (1.4×10^3)	530. – 3.9×10^4 (3.3×10^3)	12 – 2.7×10^3 (261)	421 – 3.9×10^3 (1.8×10^3)	1.0×10^4 – 6.5×10^5 (4.2×10^4)

Compound	Ashland	Jackson Hole	Rockford	Shaker Heights	Whitestown	Willoughby	Wooster
Σ PFAS	1.6×10^3 – 1.9×10^4 (7.8×10^3)	830. – 1.0×10^4 (5.2×10^3)	342 – 8.9×10^3 (1.4×10^3)	588 – 3.4×10^4 (3.4×10^3)	13 – 3.0×10^3 (275)	498 – 4.2×10^3 (1.9×10^3)	1.1×10^4 – 6.7×10^5 (4.3×10^4)

See footnotes for Table S11.

Table S13. Average and standard deviation of PFAS concentrations in blanks (ng L^{-1})

Compound	Method Blanks[a] (n = 16)	Site Blanks[b] (n = 7)	Field Blank[c] (n = 1)
1	0.002 ± 0.002	0.064 ± 0.051	0.006
2	0.002 ± 0.001	0.20 ± 0.14	0.002
3	0.020 ± 0.013	0.29 ± 0.26	0.011
4	0.002 ± 0.001	0.069 ± 0.087	0.001
5	0.051 ± 0.066	0.047 ± 0.043	n.d.[d]
6	< 0.001	0.005 ± 0.014	n.d.
7	< 0.001	0.003 ± 0.004	n.d.
8	0.008 ± 0.007	0.15 ± 0.22	0.008
9	0.001 ± 0.002	0.044 ± 0.037	n.d.
10	0.001 ± 0.004	0.003 ± 0.007	n.d.
11	0.178 ± 0.378	1.1 ± 1.0	0.88
12	0.050 ± 0.063	0.11 ± 0.16	n.d.
13	0.35 ± 0.44	0.53 ± 0.64	n.d.
14	0.22 ± 0.22	1.9 ± 1.3	1.0
15	0.005 ± 0.010	0.4 ± 1.0	n.d.
16	0.67 ± 1.68	4.4 ± 5.8	0.40
17	0.010 ± 0.010	0.021 ± 0.030	0.10
18	0.48 ± 1.25	1.6 ± 1.1	n.d.
19	0.037 ± 0.052	0.39 ± 0.93	0.18
20	0.33 ± 0.34	1.2 ± 1.2	0.42
21	0.054 ± 0.067	0.098 ± 0.097	0.05
23	0.052 ± 0.069	0.24 ± 0.23	0.12

[a] Method blanks consisted of Nanopure water carried through the entire sample preparation procedure.

[b] Site blanks were prepared by filling the HDPE collection tub with 1 L of Nanopure water and leaving the water exposed to the atmosphere on a day without rain. Accordingly, the site blanks include contributions from dry deposition but not wet deposition. Here, site blanks are averaged from Ashland (n = 2), Rockford (n = 2), Whitestown (n = 2), and Willoughby (n = 1). Site blanks were not available from Jackson Hole, Shaker Heights, or Wooster, but site blanks for all locations have been previously analyzed in Pike et al.[1]

[c] The field blank was a ride-along bottle of Nanopure water from the Whitestown site.

[d] n.d. = non-detect

Table S14. Kruskal-Wallis test comparing EPA-monitored and emerging PFAS at each sampling site

Sampling Site	***p*-value***
Shaker Heights, OH	**1.80×10^{-5}**
Jackson Hole, WY	0.333
Wooster, OH	**$< 2.20 \times 10^{-16}$**
Rockford, OH	0.968
Ashland, OH	0.350
Whitestown, IN	0.104
Willoughby, OH	**0.020**

**p*-values < 0.05 are statistically significant and bolded.

Table S15. Kruskal-Wallis test comparing chain lengths at each sampling site

Sampling Site	***p*-value***
Shaker Heights, OH	**4.00×10^{-7}**
Jackson Hole, WY	**0.018**
Wooster, OH	**3.24×10^{-9}**
Rockford, OH	0.088
Ashland, OH	**0.023**
Whitestown, IN	0.168
Willoughby, OH	**0.046**

**p*-values < 0.05 are statistically significant and bolded. Only statistically significant results were subjected to post-hoc analysis.

Table S16. Results (*p*-values) of Wilcoxon post-hoc test comparing chain lengths

Sampling Location	**Ultra-Short/Short**	**Ultra-Short/Long**	**Short/Long**
Shaker Heights, OH	**1.70×10^{-6} ***	**3.50×10^{-7}**	0.31
Jackson Hole, WY	**0.005**	**0.005**	0.958
Wooster, OH	0.100	0.130	**1.10×10^{-9}**
Ashland, OH	0.057	**0.019**	0.521
Willoughby, OH	0.196	0.316	0.078

**p*-values < 0.05 are statistically significant and bolded.

Table S17. Results of Kruskal-Wallis test comparing functional class at each sampling site

Sampling Site	***p*-value***
Shaker Heights, OH	$\mathbf{< 2.20 \times 10^{-16}}$
Jackson Hole, WY	0.072
Wooster, OH	$\mathbf{< 2.20 \times 10^{-16}}$
Rockford, OH	$\mathbf{3.17 \times 10^{-5}}$
Ashland, OH	$\mathbf{1.24 \times 10^{-9}}$
Whitestown, IN	0.834
Willoughby, OH	0.474

**p*-values < 0.05 are statistically significant and bolded. Only statistically significant results were subjected to post-hoc analysis.

Table S18. Results (*p*-values) of Wilcoxon post-hoc test comparing functional classes at each sampling site

	Shaker Heights, OH	**Wooster, OH**	**Rockford, OH**	**Ashland, OH**
FTCA/FTUCA	1.00	**9.50×10^{-6}**	1.00	0.879
FTCA/H-PFCA	**3.70×10^{-7}**	0.994	0.233	**0.002**
FTCA/H-PFdiCA	1.00	**0.013**	N/A	0.298
FTCA/oPFSA	**0.028**	**0.048**	**0.001**	**0.043**
FTCA/PFCA	**2.90×10^{-8}**	**3.50×10^{-12}**	1.00	**0.017**
FTCA/PFECA+	1.00	**4.60×10^{-8}**	1.00	1.00
FTCA/PFSA	**7.4×10^{-7}**	**3.50×10^{-12}**	1.00	1.00
FTUCA/H-PFCA	**0.001**	**1.80×10^{-5}**	0.175	**0.010**
FTUCA/H-PFdiCA	1.00	0.083	N/A	1.00
FTUCA/oPFSA	0.141	0.994	0.493	1.00
FTUCA/PFCA	**0.016**	1.00	0.700	**0.022**
FTUCA/PFECA+	1.00	0.994	1.00	0.530
FTUCA/PFSA	**0.0001**	0.055	1.00	1.00
H-PFCA/H-PFdiCA	**1.10×10^{-5}**	0.058	N/A	**0.006**
H-PFCA/oPFSA	**0.0003**	0.072	**5.70×10^{-5}**	**0.0001**
H-PFCA/PFCA	0.651	**7.30×10^{-8}**	0.666	0.879
H-PFCA/PFECA+	**0.003**	**6.30×10^{-7}**	1.00	0.567
H-PFCA/PFSA	1.00	**3.50×10^{-15}**	**0.029**	**0.006**
H-PFdiCA/oPFSA	0.376	1.00	N/A	1.00
H-PFdiCA/PFCA	**0.001**	0.076	N/A	**0.003**
H-PFdiCA/PFECA+	1.00	**0.037**	N/A	0.078
H-PFdiCA/PFSA	**1.90×10^{-5}**	**7.90×10^{-7}**	N/A	0.879
oPFSA/PFCA	**0.0002**	0.994	**0.0001**	**0.001**
oPFSA/PFECA+	1.00	0.464	0.493	**0.022**
oPFSA/PFSA	**0.001**	**0.002**	**0.013**	0.503
PFCA/PFECA+	**0.015**	0.640	1.00	1.00
PFCA/PFSA	0.066	**0.0003**	0.292	**0.020**
PFECA+/PFSA	**0.001**	0.202	1.00	0.879

p-values < 0.05 are statistically significant and bolded. N/A indicates that the comparison could not be made due to functional class not being detected at that location.

Table S19. Results of Kruskal-Wallis test comparing sampling sites in terms of functional class

Functional Class	*p*-value*
FTCA	**$< 2.20 \times 10^{-16}$**
FTUCA	**1.00×10^{-4}**
H-PFCA	**$< 2.20 \times 10^{-16}$**
H-PFdiCA	**1.44×10^{-6}**
oPFSA	**5.57×10^{-5}**
PFCA	**$< 2.20 \times 10^{-16}$**
PFECA+	**2.00×10^{-4}**
PFSA	**1.00×10^{-3}**

**p*-values < 0.05 are statistically significant and bolded. Only statistically significant results were subjected to post-hoc analysis.

Table S20. Results (*p*-values) of Wilcoxon post-hoc test comparing sampling sites in terms of functional classes

	FTCA	FTUCA	H-PFCA	H-PFdiCA	oPFSA	PFCA	PFECA+	PFSA
Shaker Heights/ Jackson Hole	0.146	N/A	**0.004**	**2.20×10^{-7}**	N/A	1.00	1.00	1.00
Shaker Heights/ Wooster	**$< 2.20 \times 10^{-16}$**	**0.001**	**$< 2.20 \times 10^{-16}$**	N/A	**0.0007**	**1.00×10^{-9}**	**0.0002**	1.00
Shaker Heights/ Rockford	1.00	1.00	0.169	N/A	0.824	**0.0005**	1.00	**3.90×10^{-6}**
Shaker Heights/ Ashland	0.172	1.00	0.860	0.660	0.610	1.00	1.00	0.267
Shaker Heights/ Whitestown	1.00	1.00	0.169	N/A	N/A	**0.0005**	1.00	**0.002**
Shaker Heights/ Willoughby	N/A	N/A	N/A	N/A	N/A	**0.002**	1.00	1.00
Jackson Hole/ Wooster	0.067	N/A	**0.002**	N/A	N/A	**0.0003**	1.00	1.00
Jackson Hole/ Rockford	0.098	N/A	0.058	N/A	N/A	0.058	1.00	0.341
Jackson Hole/ Ashland	0.209	N/A	**0.009**	N/A	N/A	1.00	1.00	1.00
Jackson Hole/ Whitestown	0.146	N/A	0.860	N/A	N/A	**0.029**	1.00	0.636
Jackson Hole/ Willoughby	N/A	N/A	N/A	N/A	N/A	0.230	1.00	1.00
Wooster/ Rockford	**$< 2.20 \times 10^{-16}$**	**0.002**	**6.20×10^{-13}**	N/A	**0.0003**	**1.20×10^{-14}**	0.078	0.094
Wooster/ Ashland	**6.30×10^{-16}**	**0.026**	**4.40×10^{-14}**	**0.0002**	**0.0005**	**2.00×10^{-7}**	0.677	1.00
Wooster/ Whitestown	**1.50×10^{-8}**	**0.133**	**2.30×10^{-9}**	N/A	N/A	**5.20×10^{-12}**	0.449	0.192
Wooster/ Willoughby	N/A	N/A	N/A	N/A	N/A	**$< 2.20 \times 10^{-16}$**	0.237	1.00
Rockford/ Ashland	0.631	1.00	**0.050**	N/A	0.216	**6.50×10^{-5}**	1.00	0.163
Rockford/ Whitestown	1.00	1.00	0.860	N/A	N/A	0.361	1.00	1.00
Rockford/ Willoughby	N/A	N/A	N/A	N/A	N/A	1.00	1.00	0.848
Ashland/ Whitestown	0.394	1.00	0.103	N/A	N/A	**0.0002**	1.00	0.584
Ashland/ Willoughby	N/A	N/A	N/A	N/A	N/A	**0.0003**	1.00	1.00
Whitestown/ Willoughby	N/A	N/A	N/A	N/A	N/A	0.454	1.00	0.728

p-values < 0.05 are statistically significant and bolded. N/A indicates that the comparison could not be made due to functional class not being detected at that location.

Table S21. PFAS pairs with statistically significant ($p < 0.05$) strong correlations ($\tau > 0.80$)

Compound Pair	**Correlation Coefficient (τ)**
All Sites	
Compound 1/Compound 2	0.86
Compound 10/Compound 13	0.91
Compound 11/Compound 13	0.83
Shaker Heights, OH	
Compound 1/TFA	0.87
Compound 1/Compound 2	0.82
Wooster, OH	
Compound 1/Compound 2	0.91
Compound 1/Compound 3	0.91
Compound 1/Compound 12	0.87
Compound 2/Compound 3	0.91
Compound 2/Compound 12	0.87
Compound 3/Compound 12	0.87
Compound 3/PFPeA	0.87
Compound 6/Compound 8	0.96
Compound 6/Compound 9	0.96
Compound 6/Compound 13	0.91
Compound 6/Compound 14	0.82
Compound 6/Compound 15	0.87
Compound 6/Compound 17	0.91
Compound 6/Compound 18	0.82
Compound 6/Compound 19	0.87
Compound 6/Compound 20	0.87
Compound 6/Compound 21	0.81
Compound 6/Compound 23	0.87
Compound 7/Compound 12	0.82
Compound 7/PFPeA	0.82
Compound 8/Compound 9	0.91
Compound 8/Compound 10	0.96
Compound 8/Compound 13	0.87
Compound 8/Compound 14	0.87
Compound 8/Compound 15	0.91
Compound 8/Compound 17	0.91
Compound 8/Compound 19	0.82
Compound 8/Compound 20	0.82
Compound 8/Compound 21	0.82
Compound 8/Compound 23	0.82
Compound 9/Compound 10	0.96
Compound 9/Compound 13	0.96
Compound 9/Compound 15	0.82
Compound 9/Compound 17	0.96

Compound Pair	Correlation Coefficient (τ)
Compound 9/Compound 18	0.87
Compound 9/Compound 19	0.91
Compound 9/Compound 20	0.91
Compound 9/Compound 21	0.91
Compound 9/Compound 23	0.91
Compound 10/Compound 13	0.91
Compound 10/Compound 14	0.82
Compound 10/Compound 15	0.87
Compound 10/Compound 17	0.91
Compound 10/Compound 18	0.82
Compound 10/Compound 19	0.87
Compound 10/Compound 20	0.87
Compound 10/Compound 21	0.87
Compound 10/Compound 23	0.87
Compound 11/Compound 14	0.91
Compound 12/PFPeA	0.82
Compound 13/Compound 18	0.91
Compound 13/Compound 19	0.96
Compound 13/Compound 20	0.96
Compound 13/Compound 21	0.96
Compound 13/Compound 23	0.96
Compound 13/PFOA	0.82
Compound 13/PFNA	0.82
Compound 14/Compound 15	0.96
Compound 14/PFHpA	0.82
Compound 16/PFOS	0.87
Compound 17/Compound 18	0.91
Compound 17/Compound 19	0.96
Compound 17/Compound 20	0.96
Compound 17/Compound 21	0.96
Compound 17/Compound 23	0.96
Compound 17/PFOA	0.82
Compound 17/PFNA	0.82
Compound 18/Compound 19	0.96
Compound 18/Compound 20	0.96
Compound 18/Compound 21	0.96
Compound 18/Compound 23	0.96
Compound 18/PFOA	0.82
Compound 18/PFNA	0.91
Compound 19/Compound 20	1.0
Compound 19/Compound 21	1.0
Compound 19/Compound 23	1.0
Compound 19/PFOA	0.87
Compound 19/PFNA	0.87

Compound Pair	Correlation Coefficient (τ)
Compound 20/Compound 21	1.0
Compound 20/Compound 23	1.0
Compound 20/PFOA	0.87
Compound 20/PFNA	0.87
Compound 21/Compound 23	1.0
Compound 21/PFOA	0.87
Compound 21/PFNA	0.87
Compound 23/PFOA	0.87
Compound 23/PFNA	0.87
Rockford, OH	
Compound 3/Compound 19	0.93
Compound 5/PFHxA	0.86
Ashland, OH	
Compound 1/TFA	0.81
Compound 1/PFHpA	0.81
Compound 1/PFOA	0.81
Compound 2/HFPO-DA	0.91
Compound 2/Compound 1	0.91
Compound 3/PFBA	0.81
Compound 3/Compound 5	0.91
Compound 3/Compound 14	0.91
Compound 3/Compound 21	0.91
Compound 5/Compound 14	0.81
Compound 5/Compound 21	0.81
Compound 8/Compound 15	0.84
Compound 9/PFHpA	0.81
Compound 9/PFOA	0.81
Compound 9/PFNA	0.81
Compound 9/PFOS	0.81
Compound 14/PFBA	0.91
Compound 14/PFHpA	0.81
Compound 14/PFOA	0.81
Compound 16/PFNA	0.81
Compound 16/PFDA	0.81
Compound 16/PFOS	0.91
Whitestown, IN	
Compound 2/Compound 20	1.0
Compound 11/TFA	1.0
Compound 11/PFBA	1.0
Compound 11/PFHxA	1.0
Compound 11/PFOA	1.0
Willoughby, OH	
Compound 1/Compound 2	0.82
Compound 4/Compound 14	0.85

Table S22. Correlations among PFAS at Wooster

Compound	Class	Chain Length
Group A		
1	FTCA	C4
2	PFCA	C3
3	FTCA	C5
12	H-PFCA	C7
Group B		
6	H-PFdiCA	C10
8	H-PFdiCA	C10
9	oPFSA	C8
10	PFECA+	C12
13	FTCA	C9
14	H-PFCA	C8
15	FTUCA	C8
17	FTCA	C10
18	H-PFCA	C9
19	FTCA	C11
20	H-PFCA	C10
21	FTCA	C12
23	FTCA	C13
PFOA	PFCA	C8
PFNA	PFCA	C9

Class abbreviations are defined in **Table S1**.

Table S23. Correlation coefficients between each compound and principal component

Compound[a]	**PC1**	**PC2**
1	**0.980**[b]	-0.053
2	**0.981**	-0.032
3	**0.983**	-0.019
4	0.028	0.163
5	0.665	-0.100
6	**0.996**	0.045
7	**0.992**	0.028
8	**0.993**	0.059
9	**0.998**	0.022
10	**0.995**	0.055
11	**0.988**	0.060
12	**0.966**	0.077
13	**0.999**	0.047
14	**0.996**	0.025
15	**0.983**	0.066
16	0.502	**-0.354**
17	**0.998**	0.050
18	**0.998**	0.025
19	**0.997**	0.049
20	**0.998**	0.027
21	**0.997**	0.045
23	**0.998**	0.031
TFA	0.750	**-0.661**
PFBA	**0.985**	-0.039
PFPeA	**0.989**	-0.020
PFHxA	**0.989**	-0.090
PFHpA	**0.988**	-0.071
PFOA	**0.970**	-0.203
PFNA	**0.982**	-0.139
PFDA	0.778	-0.162
PFOS	0.520	-0.270
HFPO-DA	0.041	**-0.336**

[a] Compounds with orange shading are strongly correlated (coefficient > 0.90) to principal component 1, and compounds with blue shading are strongly correlated to principal component 2.

[b] Bolded coefficients indicate a substantial contribution from that compound to the component.

Figure S1. Map of collection sites

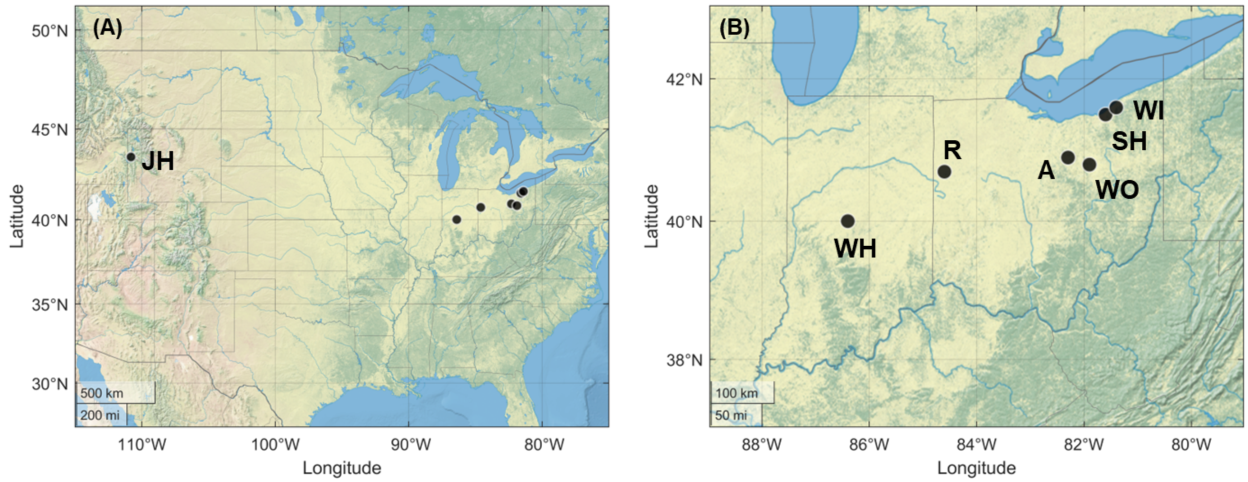


Figure S1. (A) Map showing the location of all seven collection sites: JH = Jackson Hole, WY. (B) Map of the six collection sites in the Indiana/Ohio region: WH = Whitestown, IN; R = Rockford, OH; A = Ashland, OH; WO = Wooster, OH; SH = Shaker Heights, OH; WI = Willoughby, OH.

Figure S2. Kendrick mass defect plot

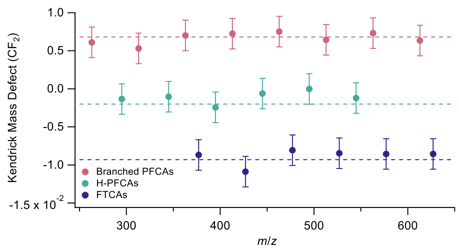


Figure S2. Kendrick mass defect plot showing homologous series of branched PFCAs (pink), H-substituted PFCAs (teal), and FTCAs (indigo) that differ by CF_2 repeating units. The Kendrick mass is calculated by multiplying the mass-to-charge ratio (*m*/*z*) of the feature of interest by the ratio of the nominal mass to the exact mass for the repeating unit in the homologous series. For CF_2, this ratio is 50/49.9968. The Kendrick mass defect is the difference between the Kendrick mass rounded to the nearest whole number and the exact Kendrick mass. Here the error bars show a tolerance of ±2 mDa. See the references by Kendrick[4] and by Bugsel and Zwiener[5] for additional information.

Figure S3. Retention times for homologous series

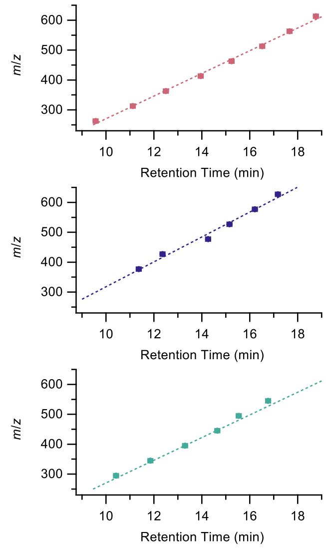


Figure S3. Plots of mass-to-charge ratio (*m*/*z*) versus retention time for the homologous series of (A) branched PFCAs, (B) FTCAs, and (C) H-substituted PFCAs. The error bars represent an uncertainty of ±0.1 minutes to match the tolerance of the MS-DIAL analysis.

Figure S4. Extracted ion chromatograms for PFOA

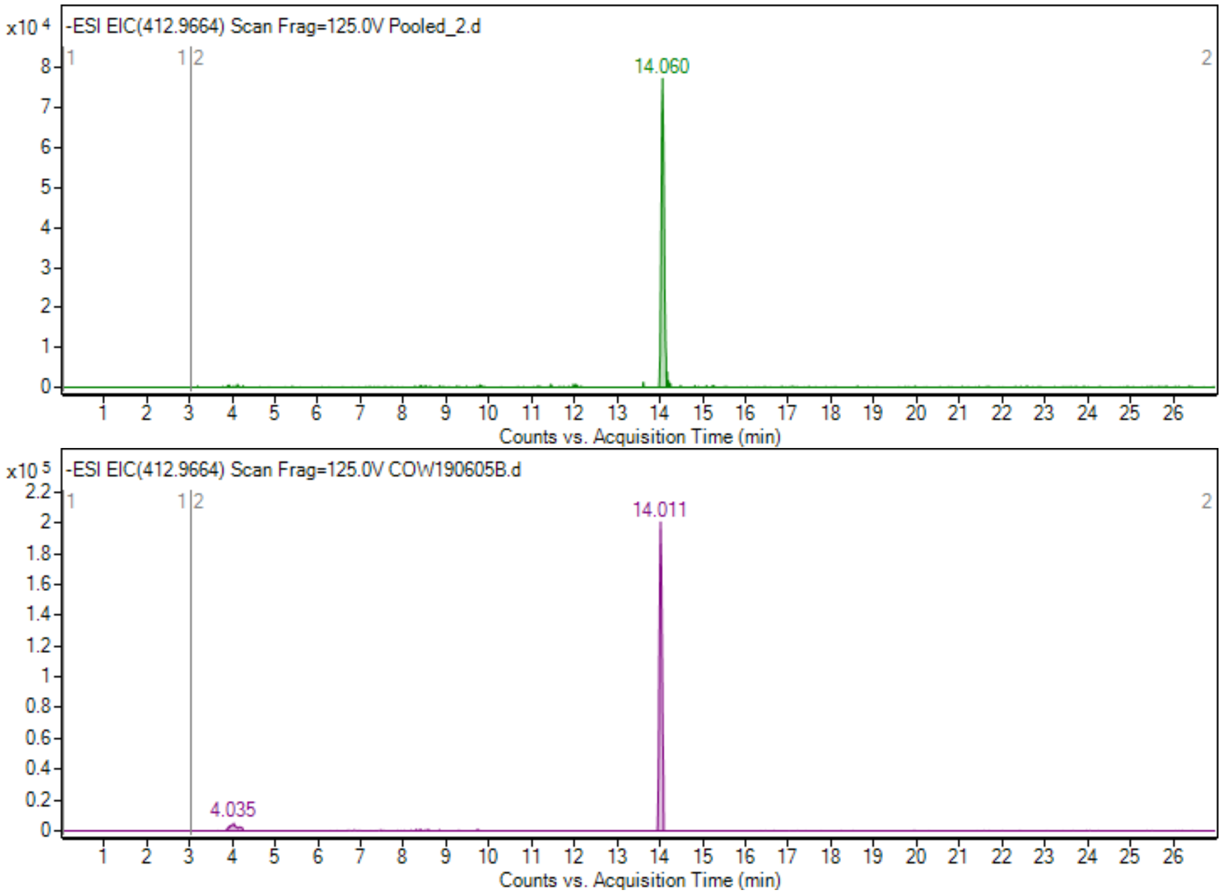


Figure S4. Extraction ion chromatograms for PFOA (perfluorooctanoic acid, *m*/*z* = 412.9964) for the pooled sample (top) and the Wooster sample collected 5 June 2019 (bottom).

Figure S5. Extracted ion chromatograms for PFHxS

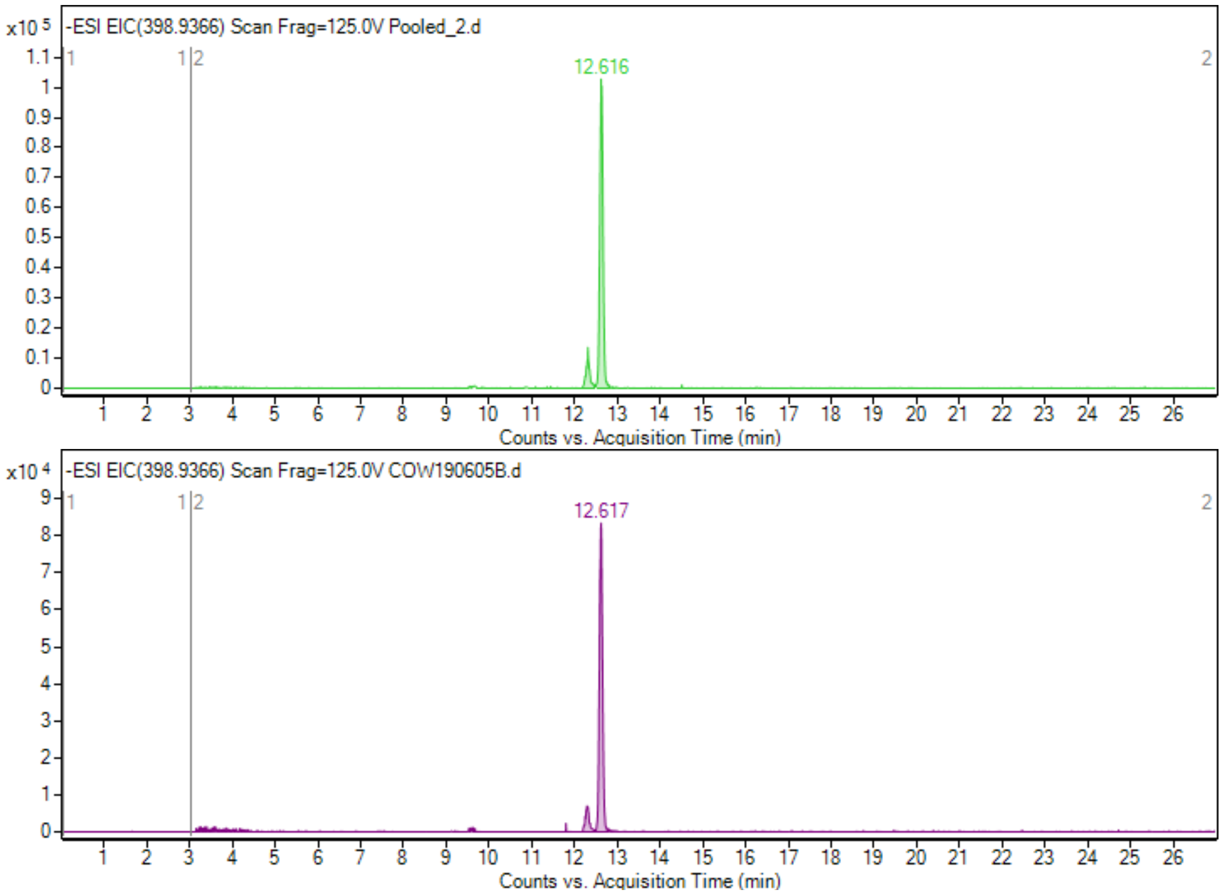


Figure S5. Extraction ion chromatograms for PFHxS (perfluorohexane sulfonic acid, m/z = 398.9366) for the pooled sample (top) and the Wooster sample collected 5 June 2019 (bottom).

Figure S6. Literature comparison of FTCAs and FTUCAs in precipitation

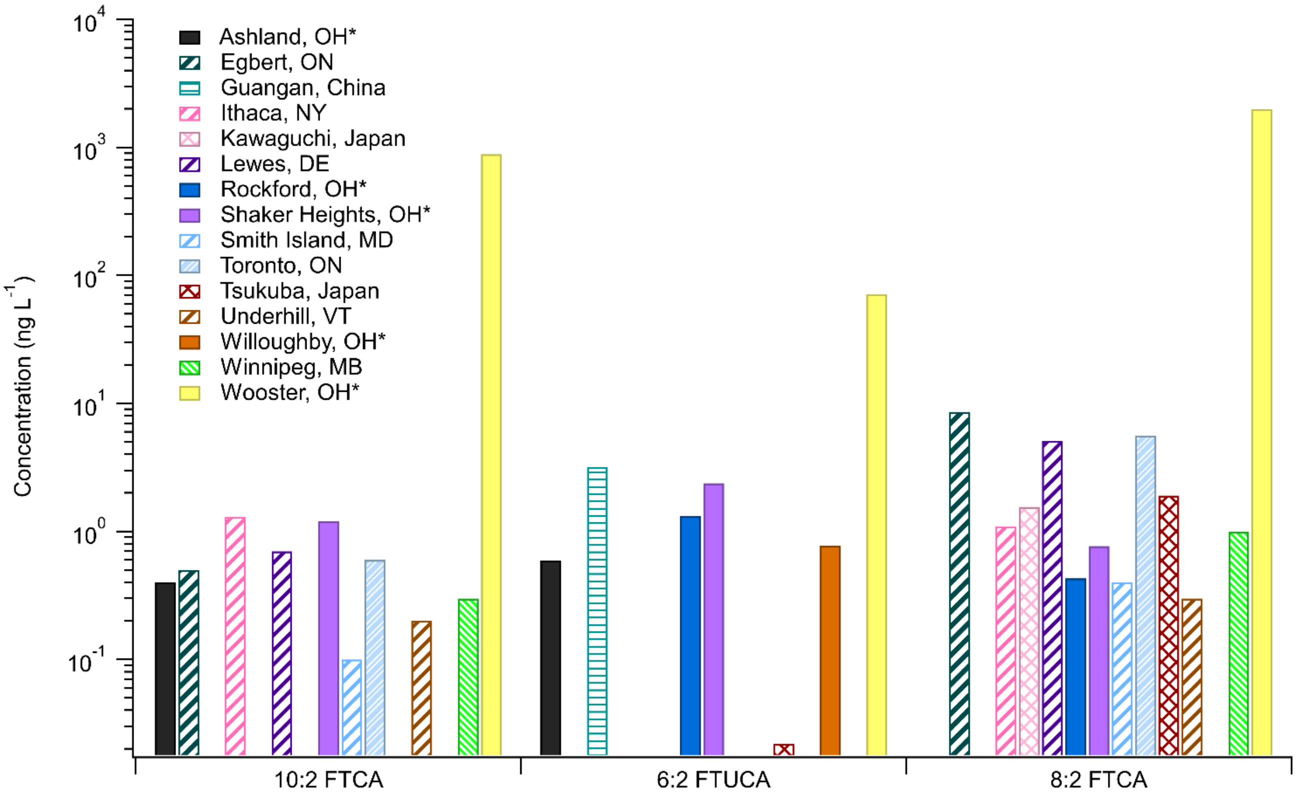


Figure S6. Comparison of the maximum concentrations of 10:2 FTCA, 6:2 FTUCA, and 8:2 FTCA measured in rainfall between 1999 and the present. The Smith Island, Maryland; Lewes, Delaware; Ithaca, New York; and Underhill, Vermont sites in the U.S. were sampled by Scott et al.[6] in 1999. The Egbert and Toronto, Ontario sites in Canada were sampled by Scott et al.[6] in 2002. The Winnipeg, Manitoba site was sampled by Loewen et al.[7] in 2004. The Tsukuba and Kawaguchi, Japan sites were sampled by Taniyasu et al.[8] in 2007. The Guangan, Sichuan site in China was sampled by Zhao et al.[9] in 2010. Sites labelled with an asterisk were sampled by Pike et al.[1] in 2019 and analyzed in this work.

Figure S7. Boxplot of PFAS deposition flux by chain length grouping and site

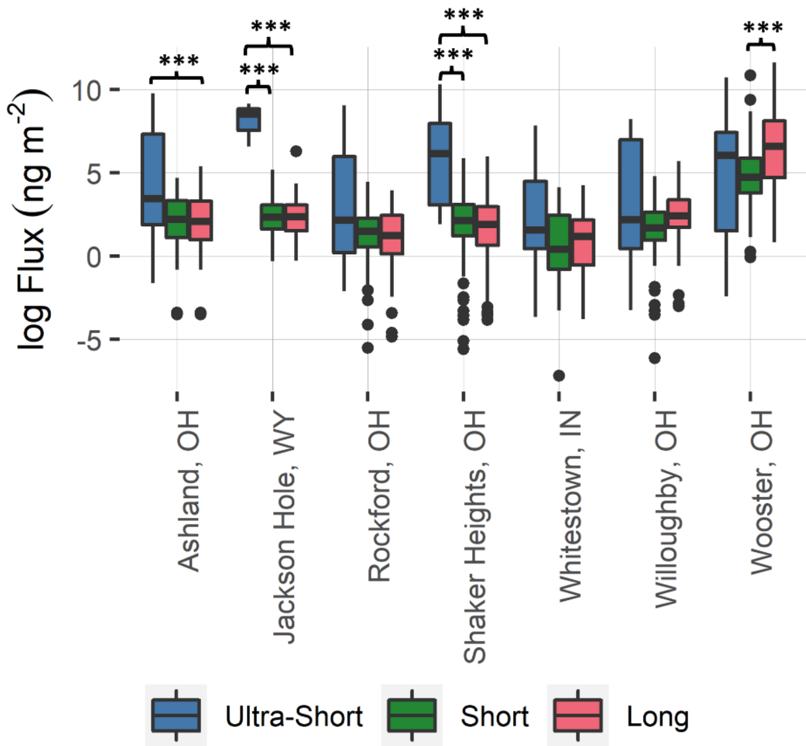


Figure S7. Boxplot comparing log flux (in ng m^{-2}) of differing chain length PFAS at each sampling site. Black asterisks indicate statistically different ($p < 0.05$) fluxes of chain lengths at that site.

Figure S8. Boxplot of PFAS deposition flux comparing functional class within site.

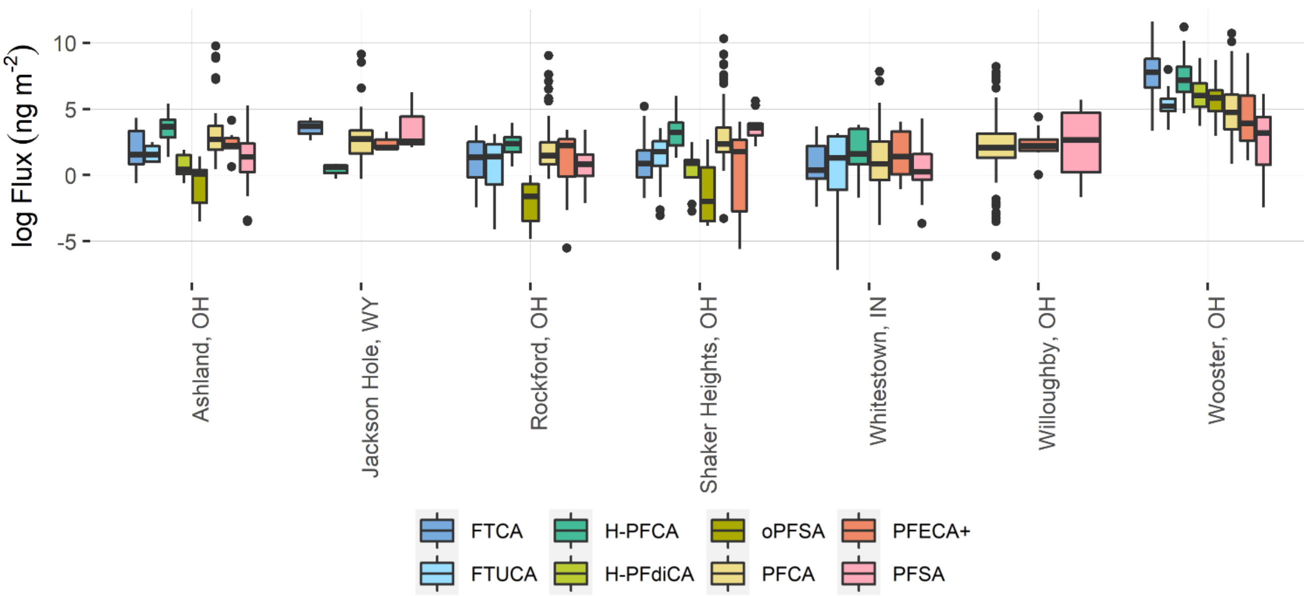


Figure S8. Boxplot comparing log flux (in ng m^{-2}) of different functional classes of PFAS at each sampling site. See **Table S17** for statistically significant comparisons. From left to right, the classes are FTCAs (light blue), FTUCAs (light cyan), H-PFCAs (mint), H-PFDiCAs (pear), oPFSAs (olive), PFCAs (light yellow), PFECAs+ (orange), and PFSAs (pink). Acronyms are defined in **Table S1**.

Figure S9. Boxplot of PFAS deposition flux comparing sites within each functional class

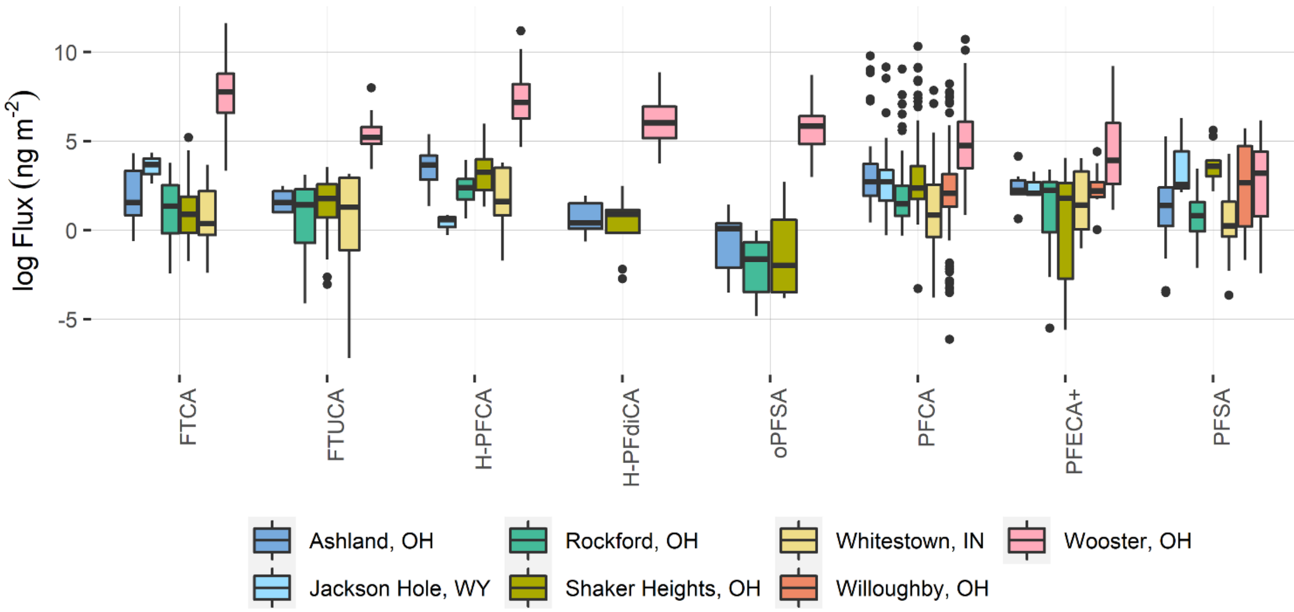


Figure S9. Boxplot comparing log flux (in ng m^{-2}) at each sampling site in terms of PFAS functional class. See **Table S19** for statistically significant comparisons. From left to right, the sites are Ashland, OH (light blue); Jackson Hole, WY (light cyan); Rockford, OH (mint); Shaker Heights, OH (olive); Whitestown, IN (light yellow); Willoughby, OH (orange); and Wooster, OH (pink). Acronyms are defined in **Table S1**.

Figure S10. Scree plot

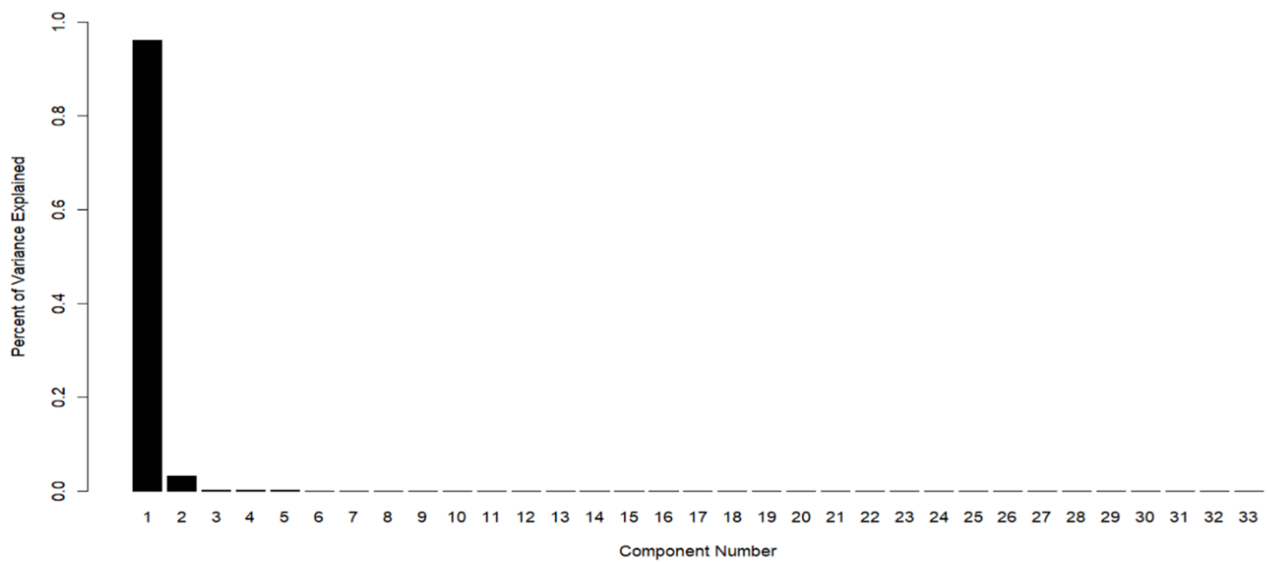


Figure S10. Scree plot for principal component analysis.

Figure S11. Principal component analysis

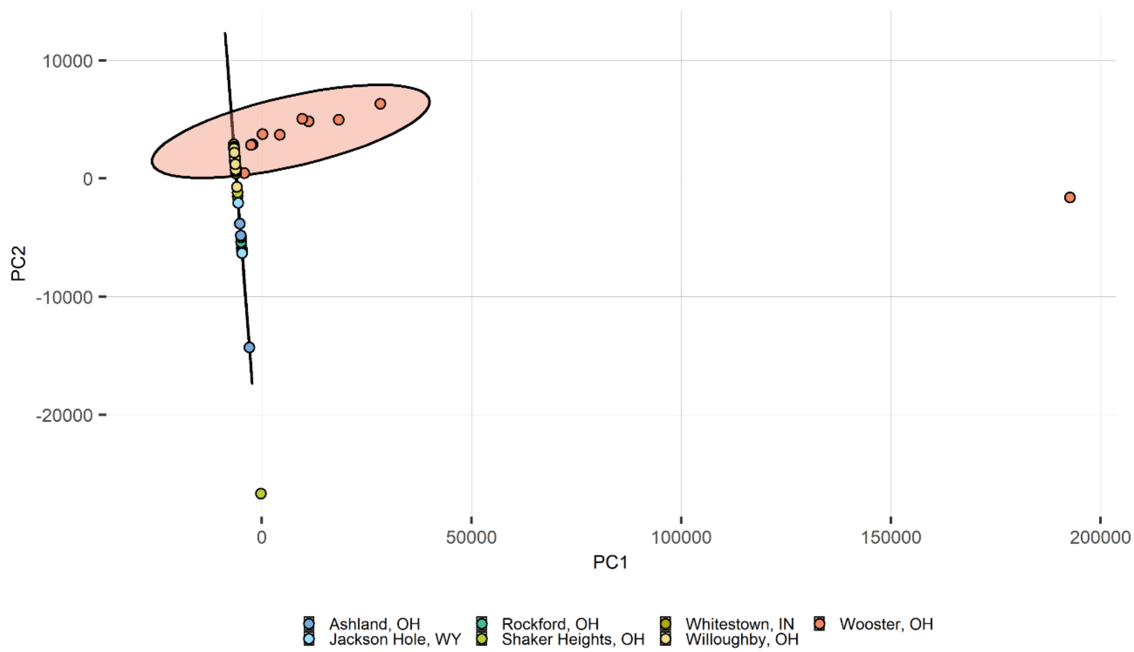
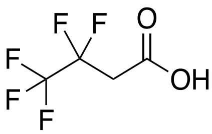
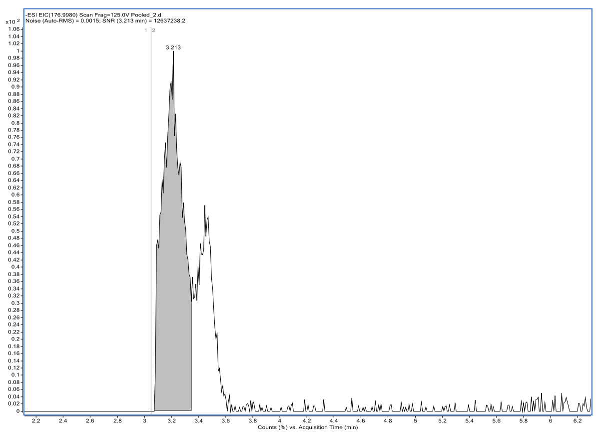


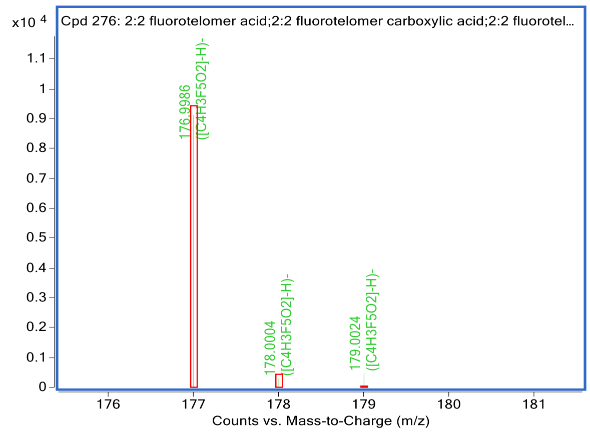
Figure S11. Principal component analysis of estimated PFAS deposition fluxes from each rainwater sample. The outlier on the far right is the 6 July 2019 sample from Wooster, OH. Data points are colored by sampling site: Ashland, OH (light blue); Jackson Hole, WY (light cyan); Rockford, OH (mint); Shaker Heights, OH (olive); Whitestown, IN (light yellow); Willoughby, OH (orange); and Wooster, OH (pink).

Appendix A: LC-MS/MS Data for Qualified Emerging PFAS (Table 1)

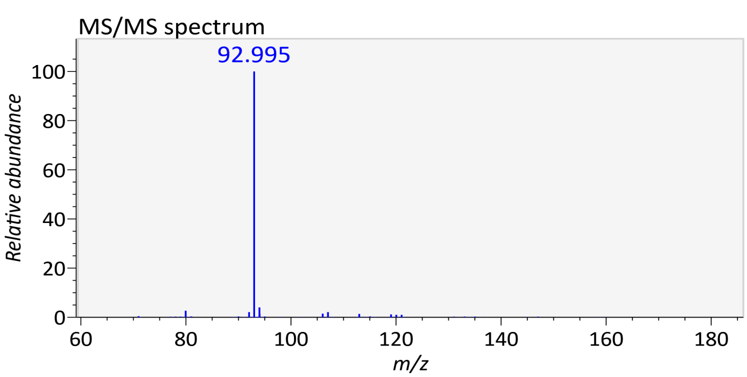
Compound 1: 2:1 FT carboxylic acid







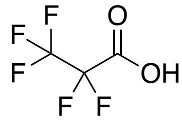
Retention time: 3.21 min

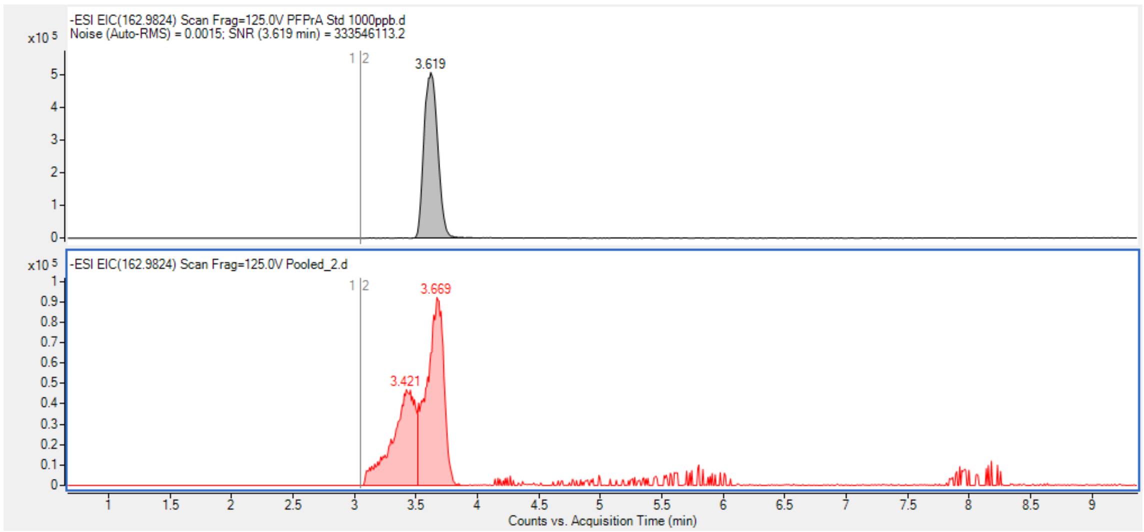


CE= 40V

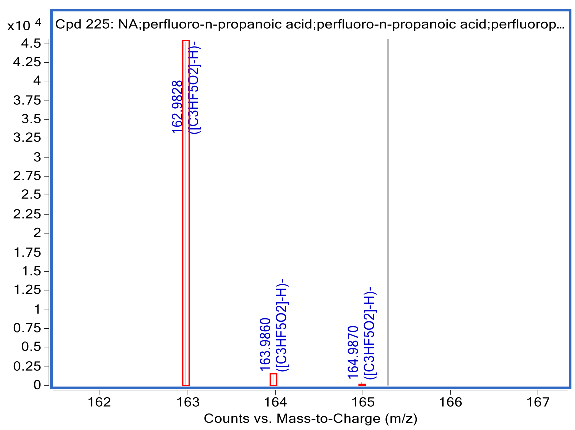
MS/MS ion (m/z)	Molecular formula	Match
92.995	$C_3F_3^-$	Fluoromatch Library

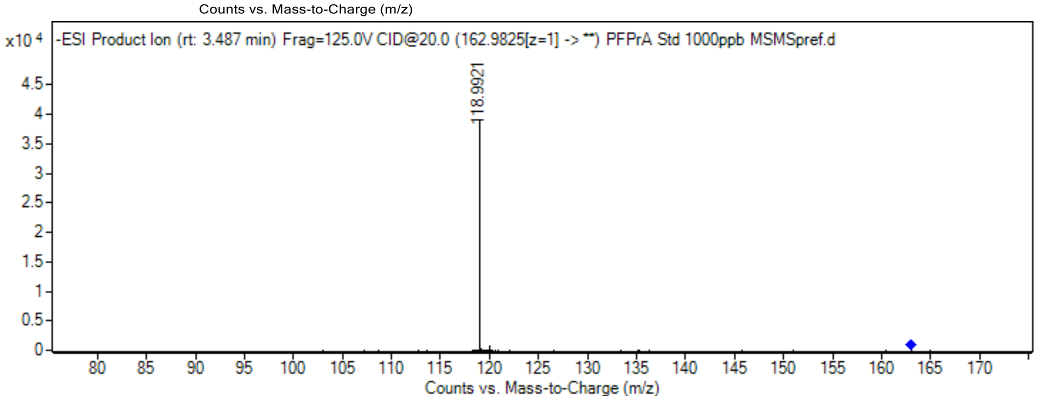
Compound 2: Perfluoropropionic acid





Top: chromatogram of standard; Bottom: Chromatogram of pooled sample

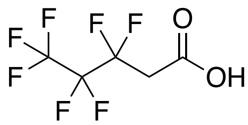


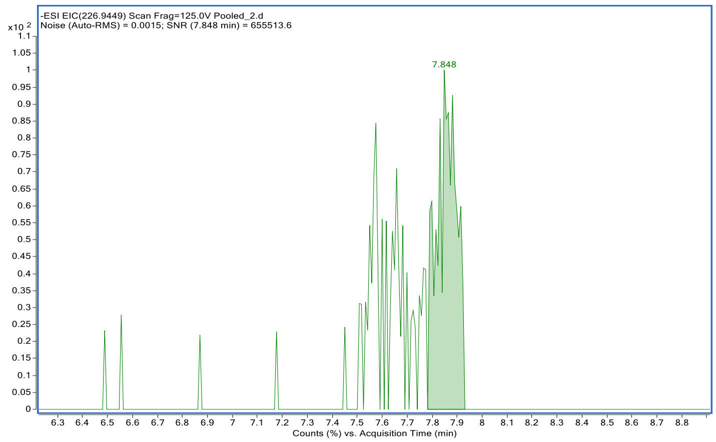


CE = in source fragmentation and 20V

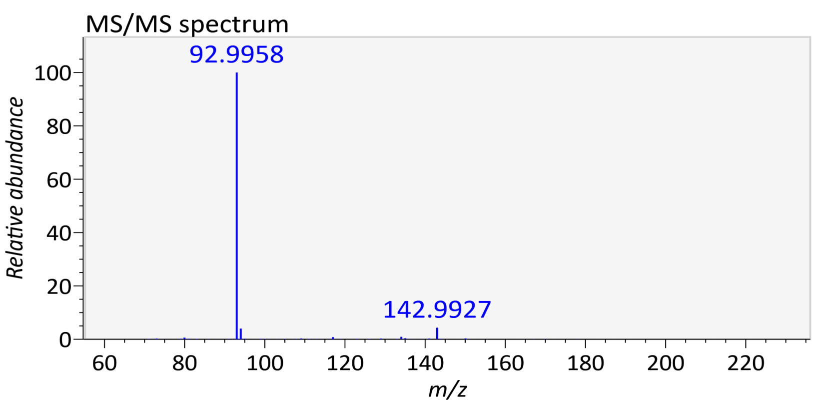
MS/MS ion (m/z)	Molecular formula	Match
118.9933	$C_2F_5^-$	Standard

Compound 3: 3:1 FT carboxylic acid (n=3)





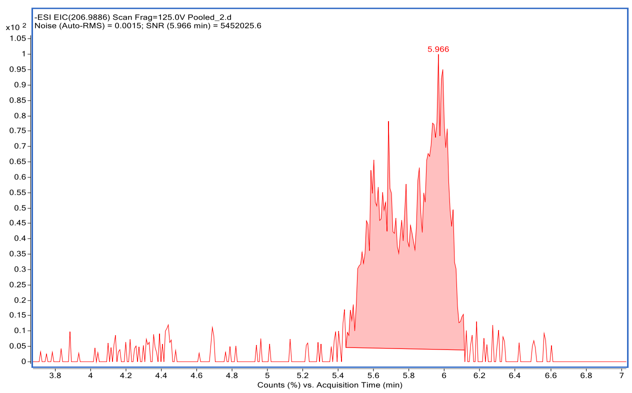
abundance too low for isotopic profile

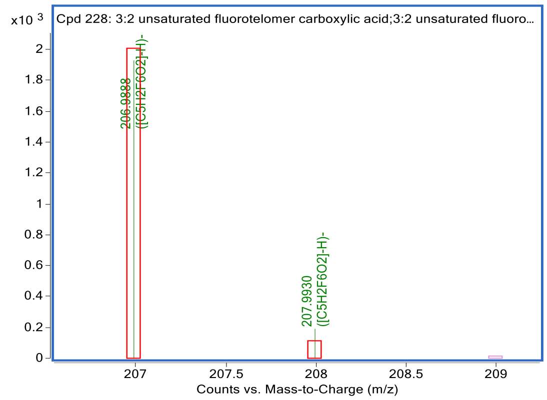


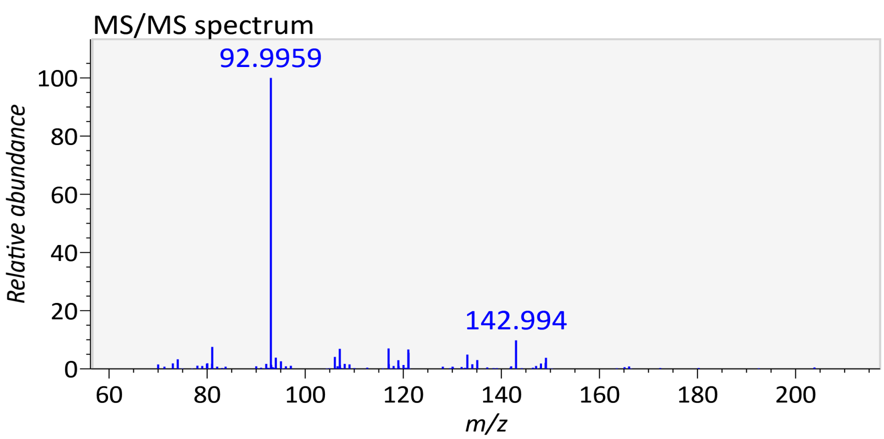
CE= 40V

MS/MS ion (m/z)	Molecular formula	Match
92.9958	$C_3F_3^-$	-
142.9927	$C_4F_3^-$	Fluoromatch Library

Compound 4:PFCA-perfluoroalkyl-Hsubstituted-1DB (n=2)



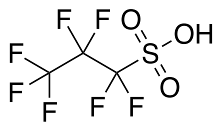




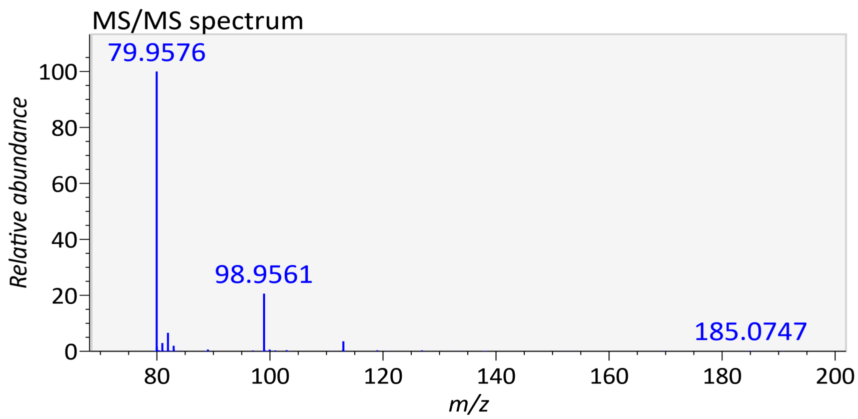
CE = 40V

MS/MS ion (m/z)	Molecular formula	Match
92.9958	$C_3F_3^-$	-
142.9927	$C_4F_3^-$	Fluoromatch Library

Compound 5: Perfluoropropane sulfonate



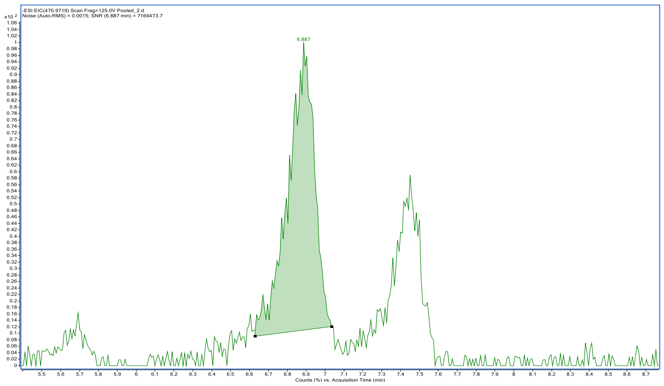
Abundance too low for accurate isotopic profile or chromatogram

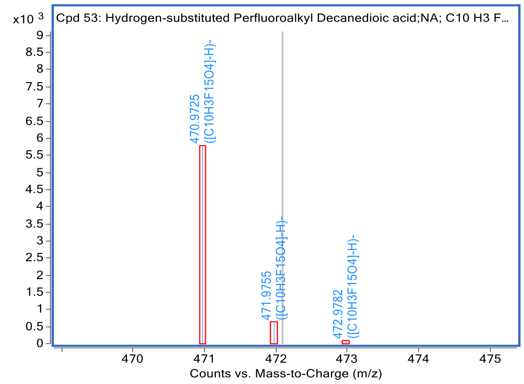


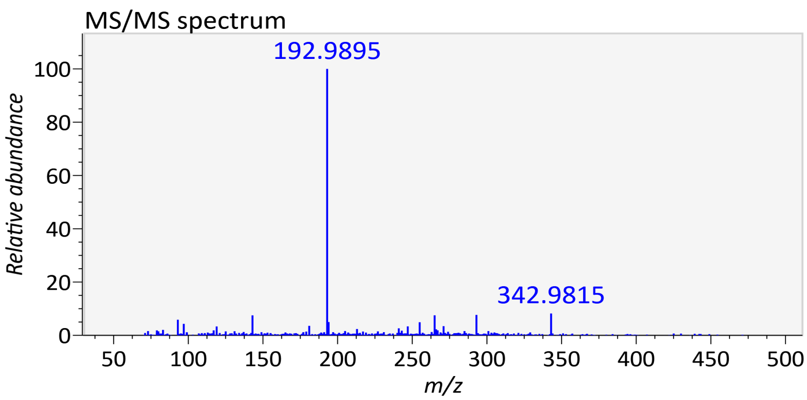
CE = 40V

MS/MS ion (m/z)	Molecular formula	Match
79.9576	SO_3^-	Fluoromatch Library
98.9561	FSO_3^-	Fluoromatch Library

Compound 6: bH-substituted perfluoroalkyl dioic acid (n=7)



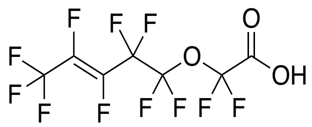


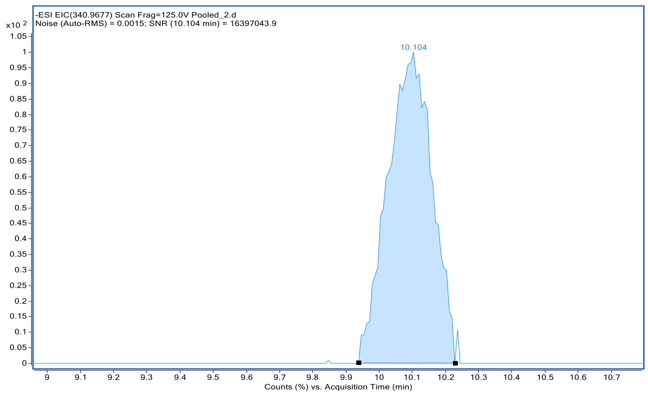


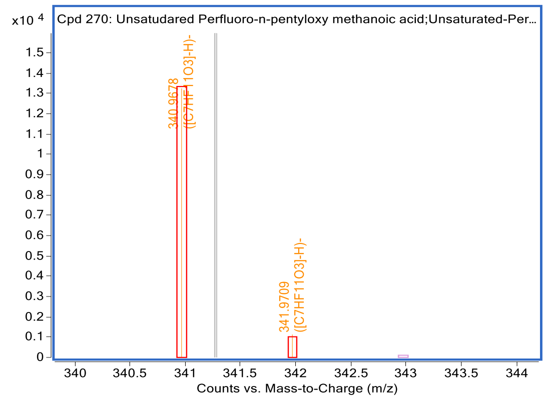
CE= 40V

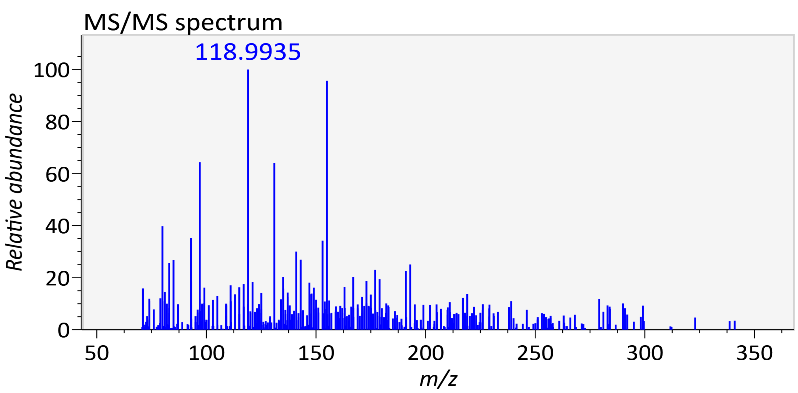
MS/MS ion (m/z)	Molecular formula	Match
192.9895	$C_5F_7^-$	-
292.9837	$C_7F_{11}^-$	Fluoromatch Library
342.9815	$C_8F_{13}^-$	Fluoromatch Library

Compound 7: unsaturated-ether-PFCA (n=2)





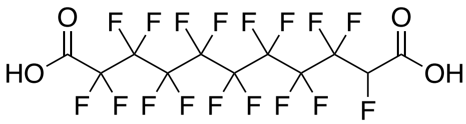


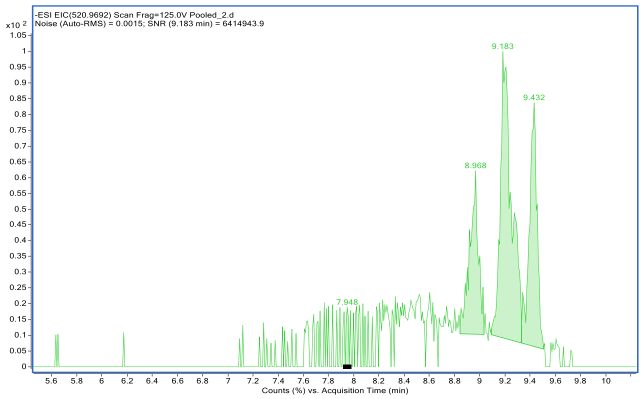


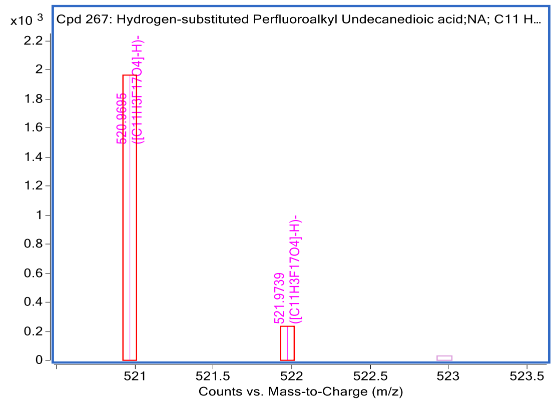
CE = 40V

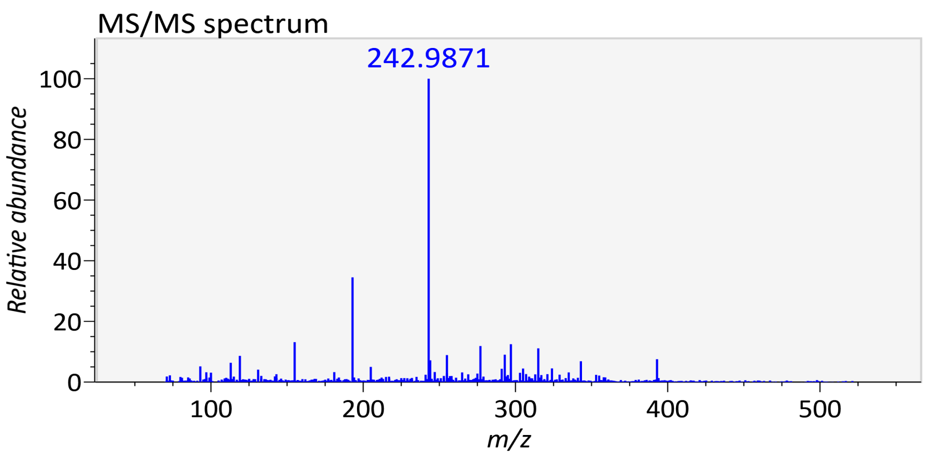
MS/MS ion (m/z)	Molecular formula	Match
118.9933	$C_2F_5^-$	Fluoromatch Library

Compound 8: H-substituted perfluoroalkyl dioic acid(n=8)





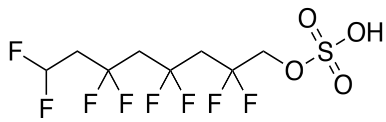


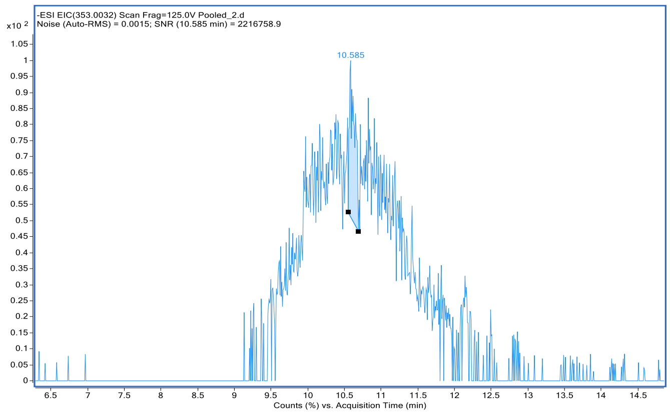


CE= 40V

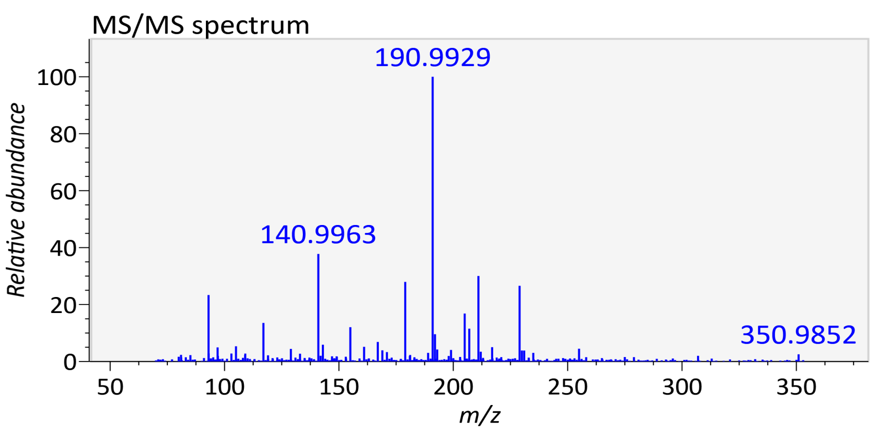
MS/MS ion (m/z)	Molecular formula	Match
192.9895	$C_5F_7^-$	-
242.9871	$C_6F_9^-$	Fluoromatch Library

Compound 9: OPFC-perfluoroalkyl sulfate (n=4)





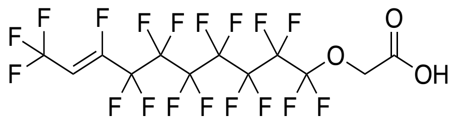
Abundance too low for accurate isotopic profile

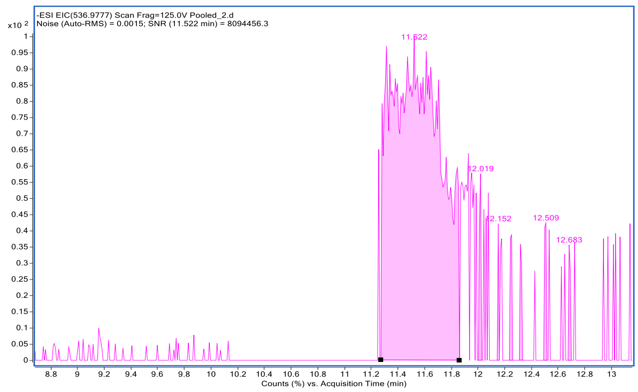


CE= 40V

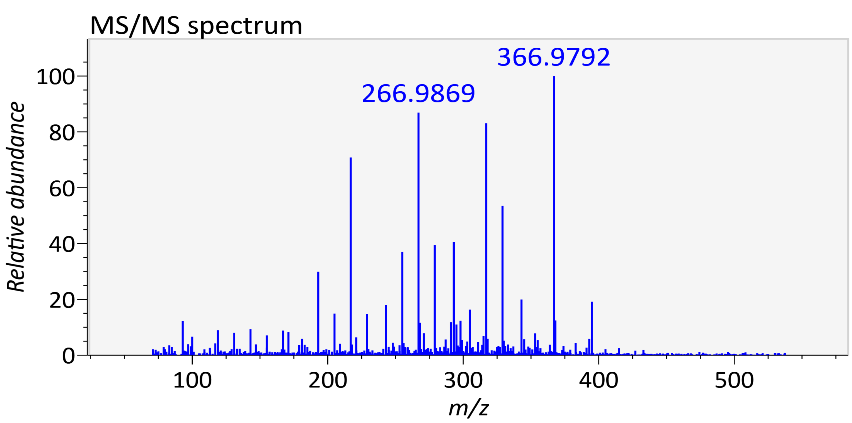
MS/MS ion (m/z)	Molecular formula	Match
204.9903	$C_6F_7^-$	Fluoromatch Library

Compound 10: H-substituted-unsaturated ether -PFCA (n=7)





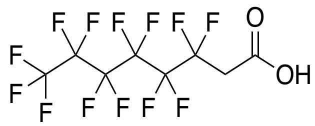
too low

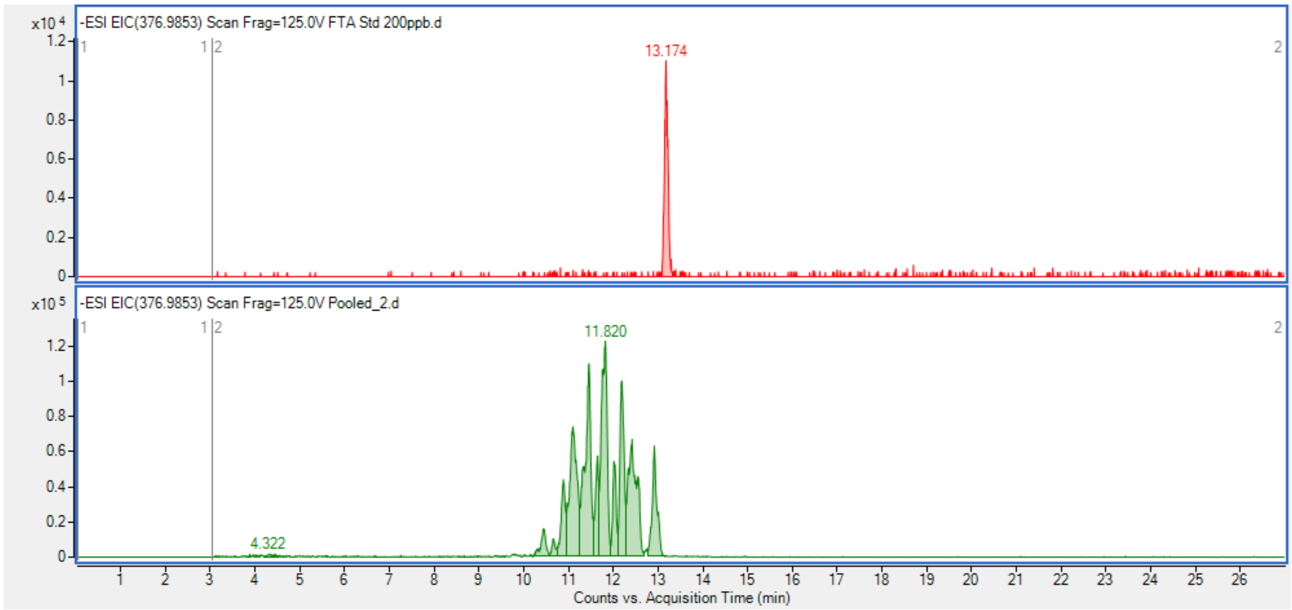


CE= 40V

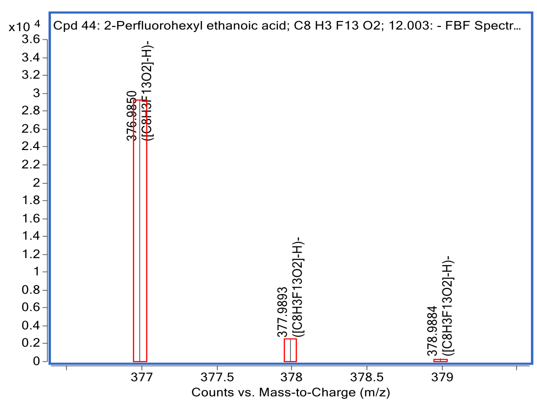
MS/MS ion (m/z)	Molecular formula	Match
192.9895	$C_5F_7^-$	Fluoromatch Library
242.9871	$C_6F_9^-$	Fluoromatch Library
292.9826	$C_7F_{11}^-$	Fluoromatch Library

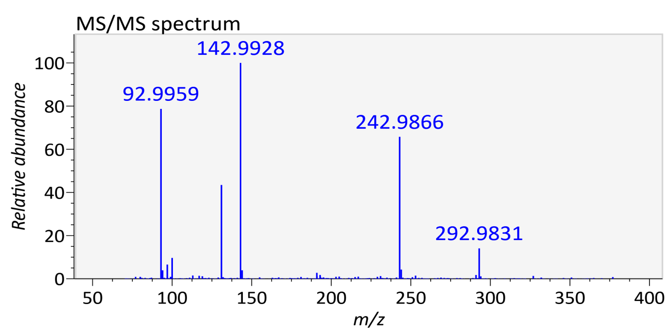
Compound 11: 6:1 FT carboxylic acid (n=6)





Top: Linear standard 2-perfluorohexyl ethanoic acid (6:2 FTCA): Bottom: Pooled sample

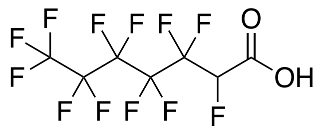


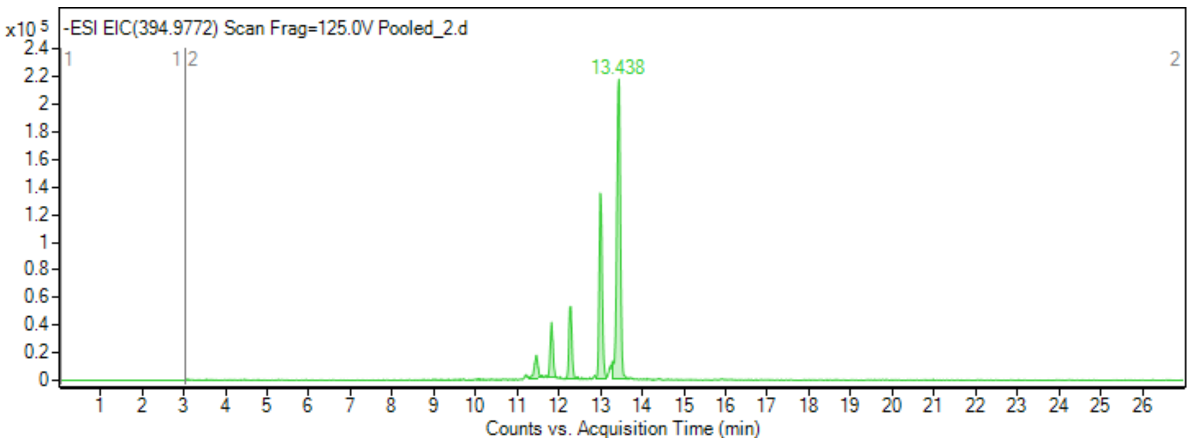


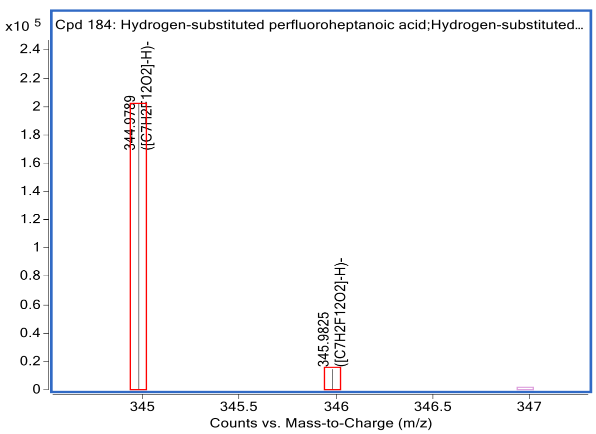
CE= in source fragmentation and 40V

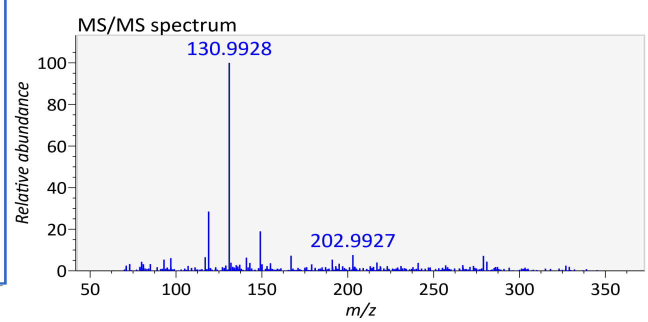
MS/MS ion (m/z)	Molecular formula	Match
92.9959	$C_3F_3^-$	-
142.9928	$C_4F_5^-$	Standard
242.9866	$C_6F_9^-$	Standard
292.9831 (in source)	$C_7F_{11}^-$	Standard

Compound 12: H-substituted-PFCA (n=5)





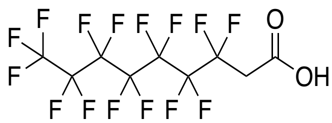


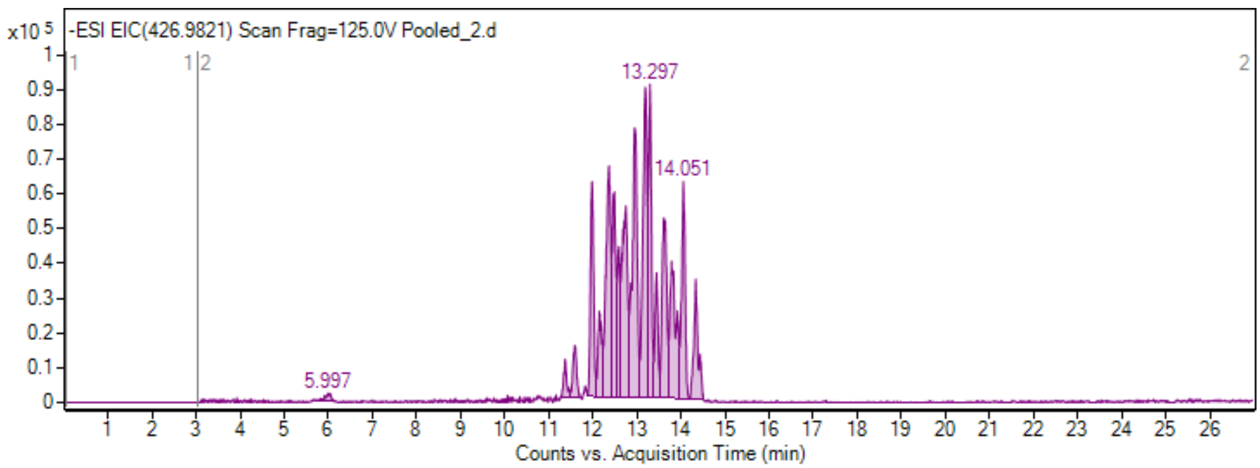


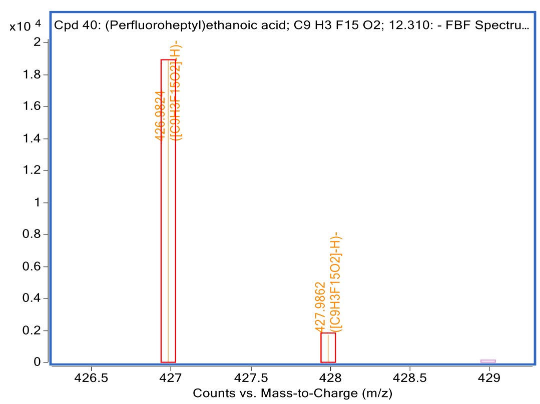
CE = in source fragmentation and 40V

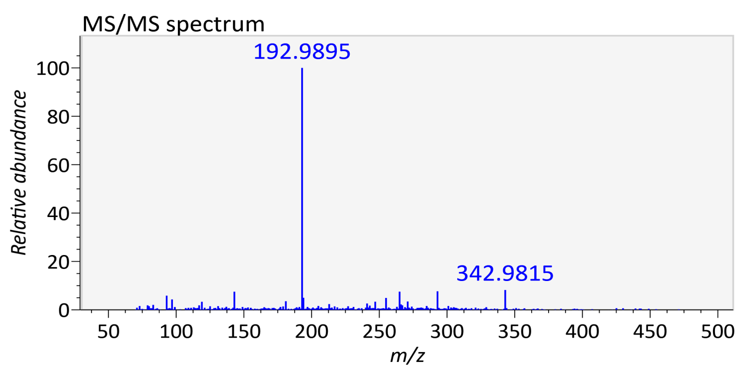
MS/MS ion (m/z)	Molecular formula	Match
118.9933	$C_2F_5^-$	Fluoromatch Library
280.9828 (in source)	$C_6F_{11}^-$	-

Compound 13: 7:2 FT carboxylic acid (n=7)





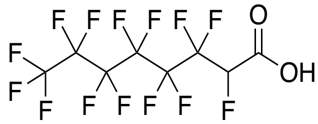


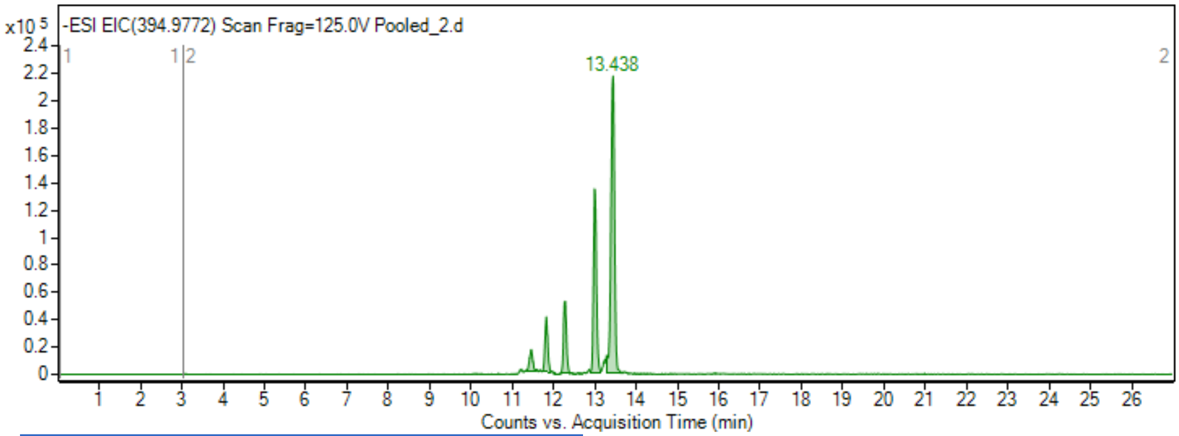


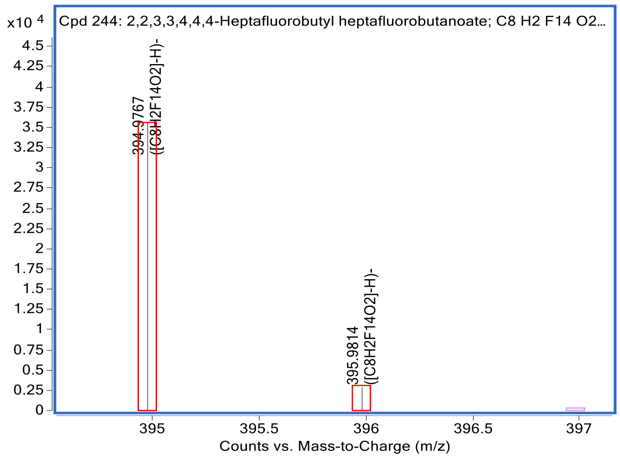
CE= in source fragmentation and 40V

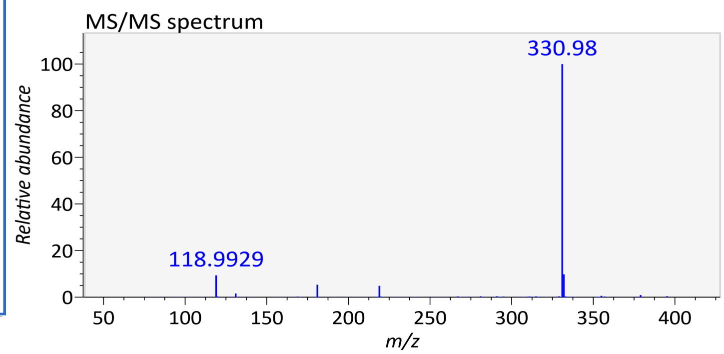
MS/MS ion (m/z)	Molecular formula	Match
192.9895	$C_5F_7^-$	Fluoromatch Library
342.9815 (in source)	$C_7F_{11}^-$	Fluoromatch Library

Compound 14: H-substituted PFCA (n=6)





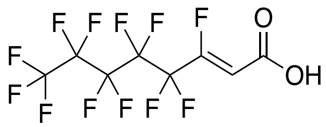


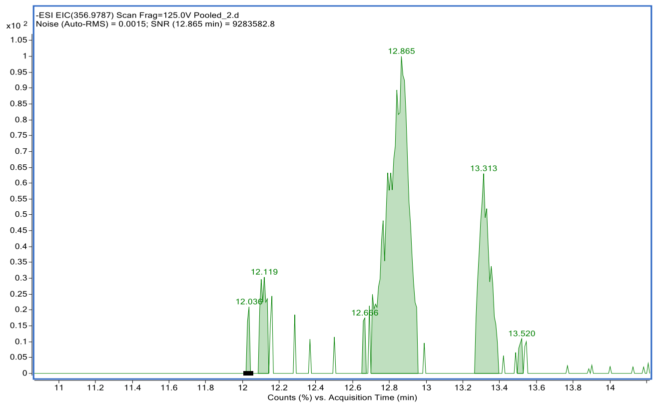


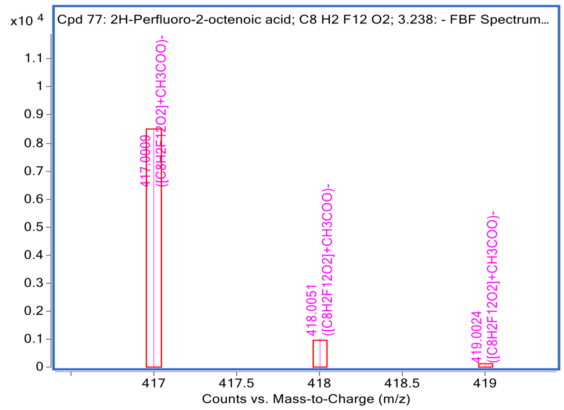
CE = in source fragmentation and 40V

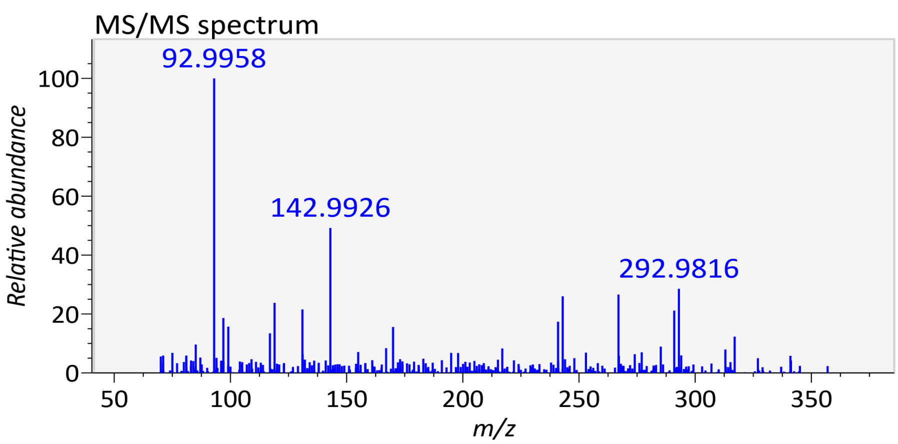
MS/MS ion (m/z)	Molecular formula	Match
118.9933	$C_2F_5^-$	-
330.9800 (in source, 40V)	$C_7F_{13}^-$	Fluoromatch Library

Compound 15: PFCA-perfluoroalkyl-Hsubstituted-1DB (n=5)





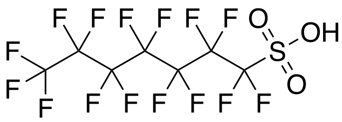


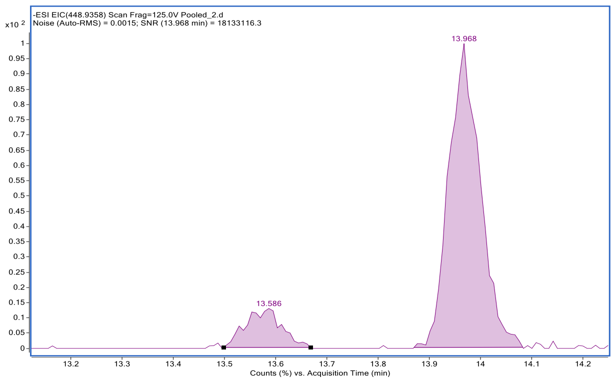


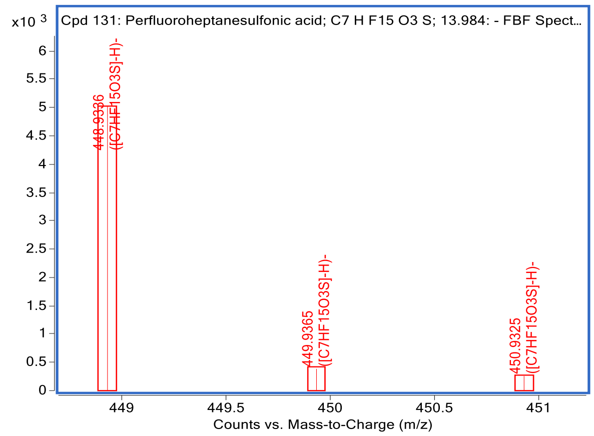
CE= in source fragmentation and 40V

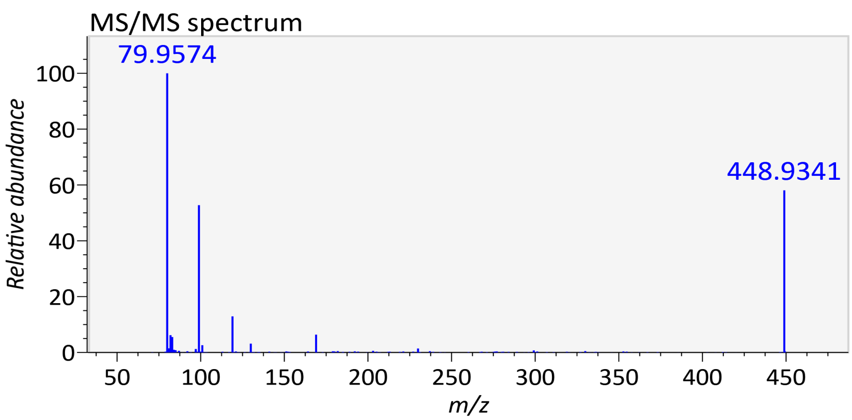
MS/MS ion (m/z)	Molecular formula	Match
92.9958	$C_3F_3^-$	-
142.9926	$C_4F_5^-$	-
292.9816	$C_7F_{11}^-$	Fluoromatch Library

Compound 16: Perfluoroalkyl sulfonate (n=7)





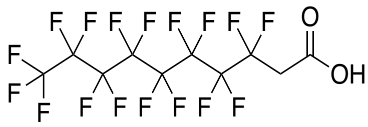


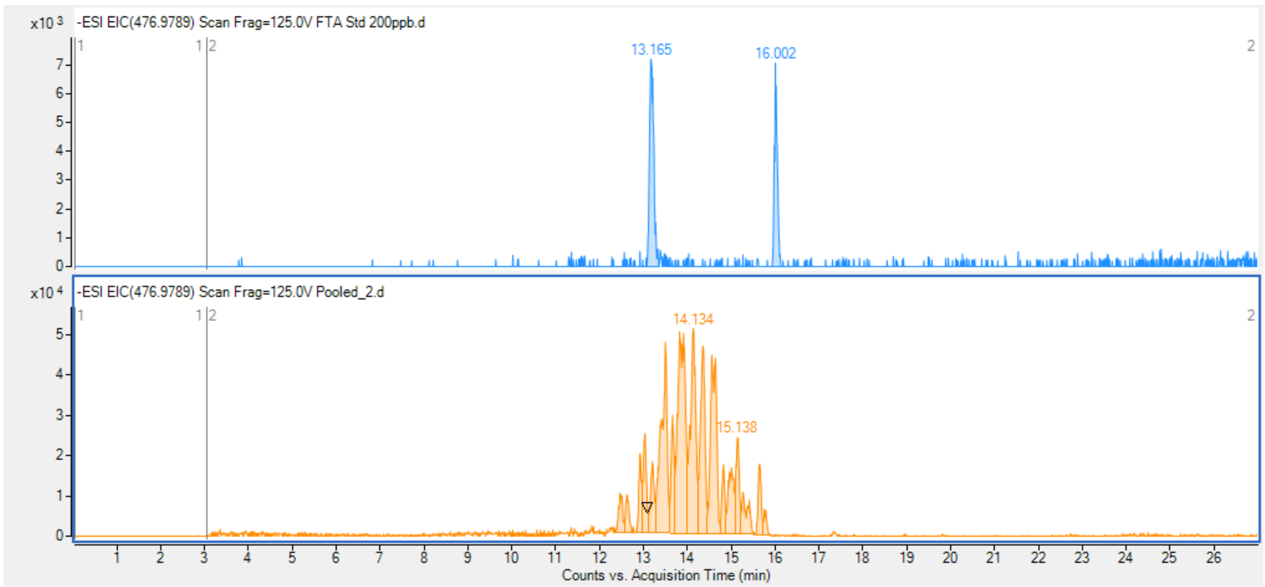


CE = 40V

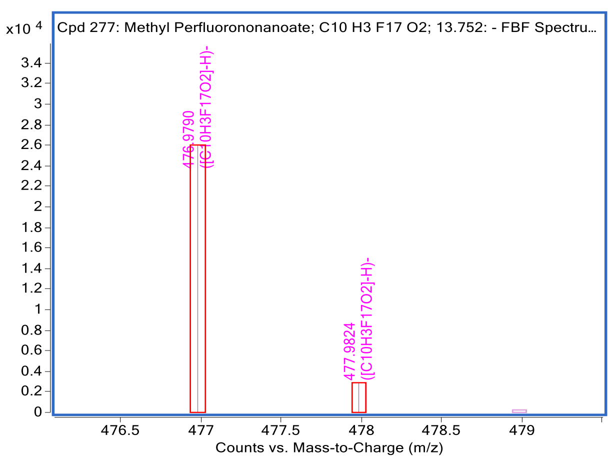
MS/MS ion (m/z)	Molecular formula	Match
79.9574	SO_3^-	Fluoromatch Library
98.9563	FSO_3^-	-
118.9931	$C_2F_5^-$	Fluoromatch Library

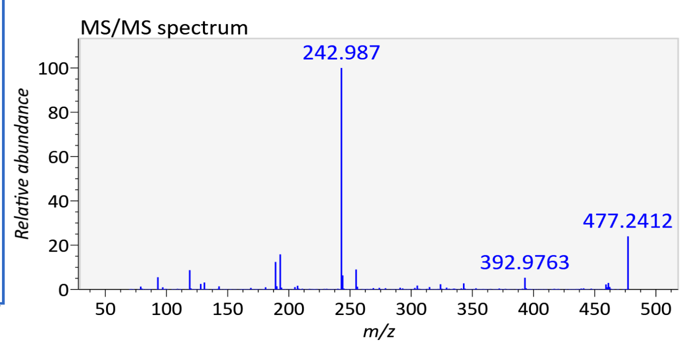
Compound 17: 8:1 FT carboxylic acid (n=8)





Top: Linear/branched standard 2-perfluorooctyl ethanoic acid (8:2 FTCA): Bottom: Pooled sample

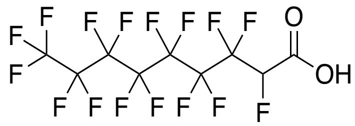


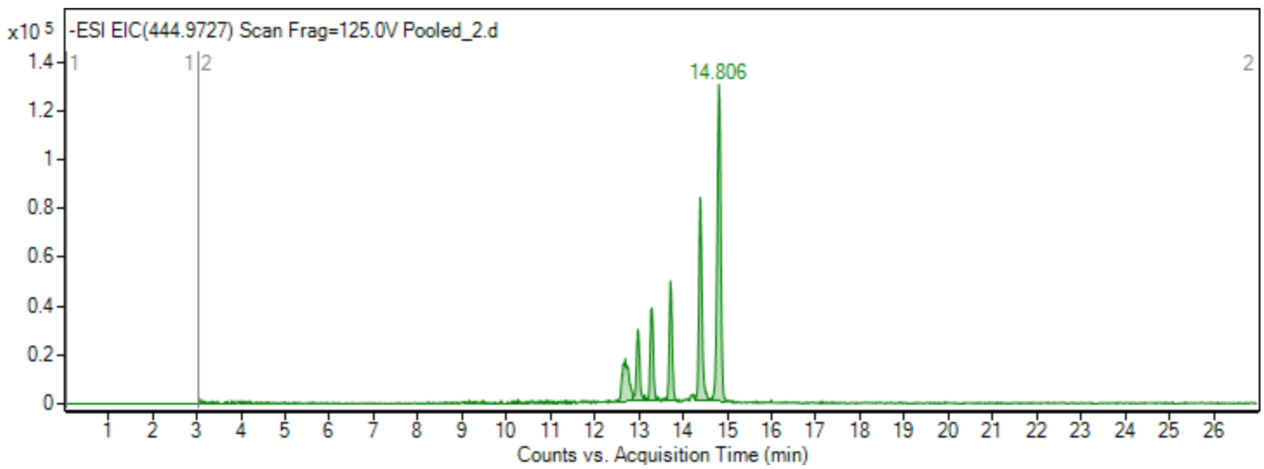


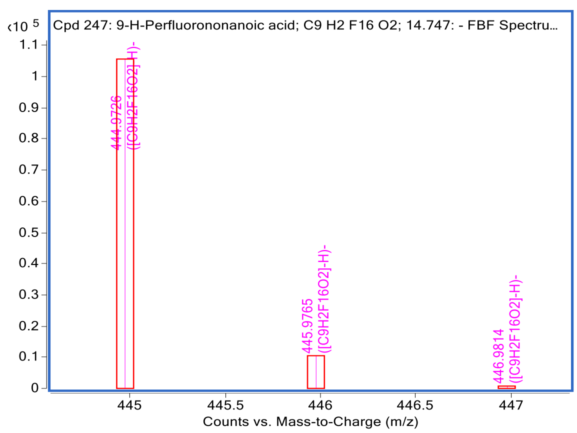
CE= in source fragmentation and 40V

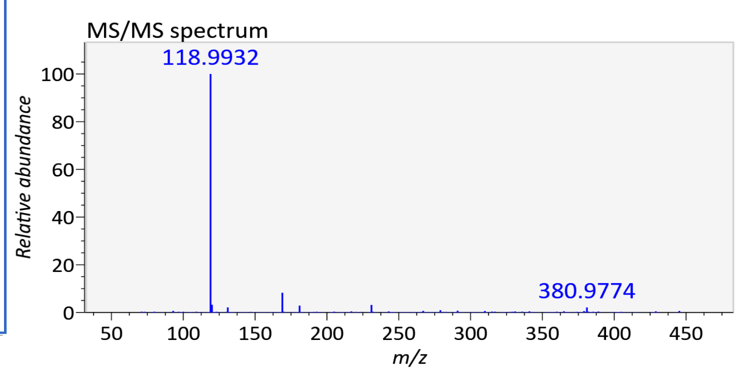
MS/MS ion (m/z)	Molecular formula	Match
118.9931	$C_2F_5^-$	Standard
242.9870	$C_6F_9^-$	Standard
392.9763 (in source)	$C_9F_{11}^-$	Standard

Compound 18: H-substituted-PFCA (n=7)





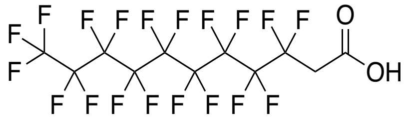


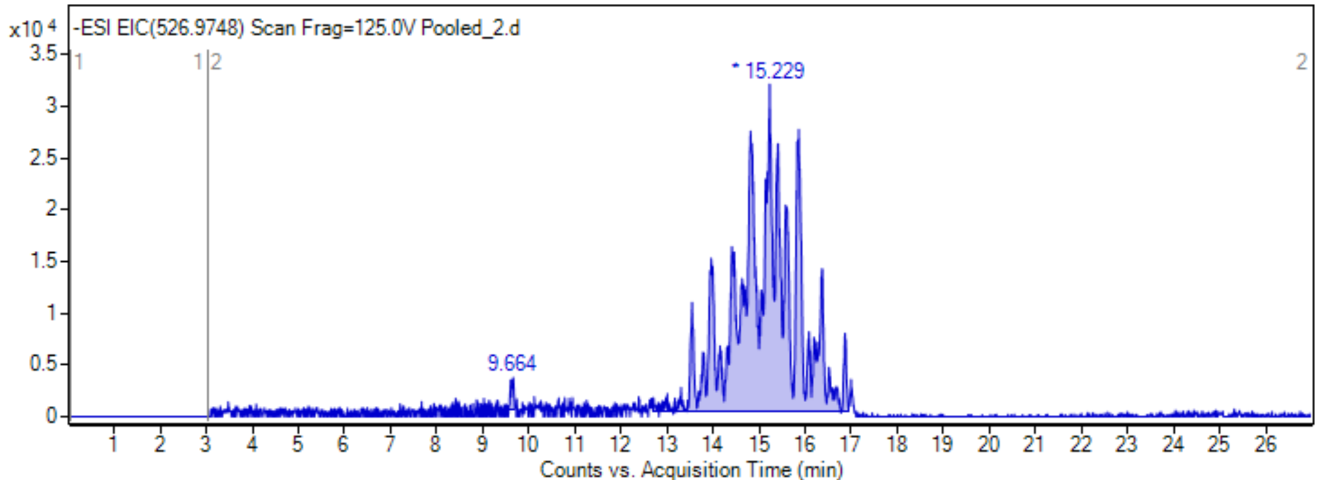


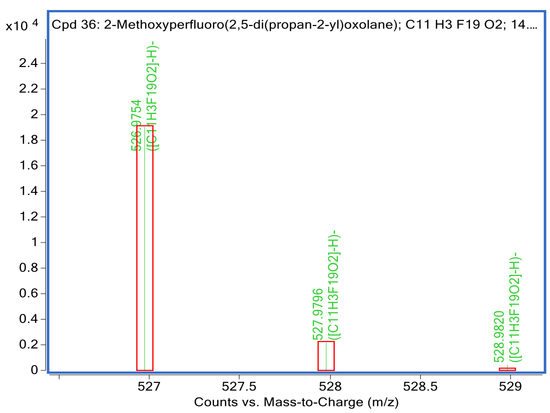
CE= in source fragmentation and 40V

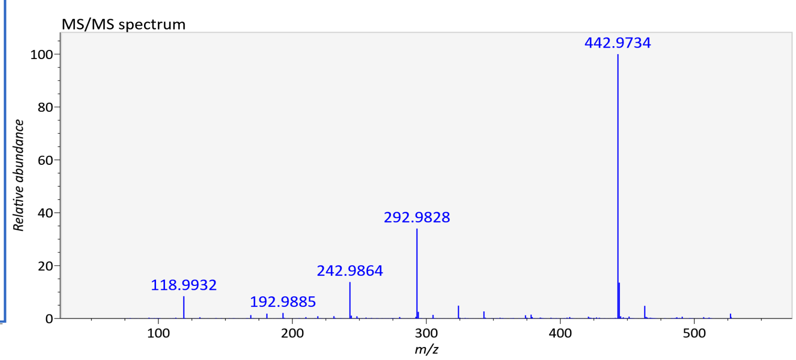
MS/MS ion (m/z)	Molecular formula	Match
118.9932	$C_2F_5^-$	Fluoromatch Library
380.9774 (in source)	$C_8F_{15}^-$	-

Compound 19: 9:1 FT carboxylic acid (n=9)





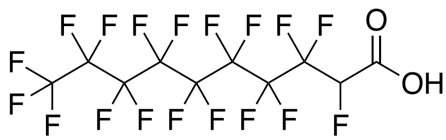


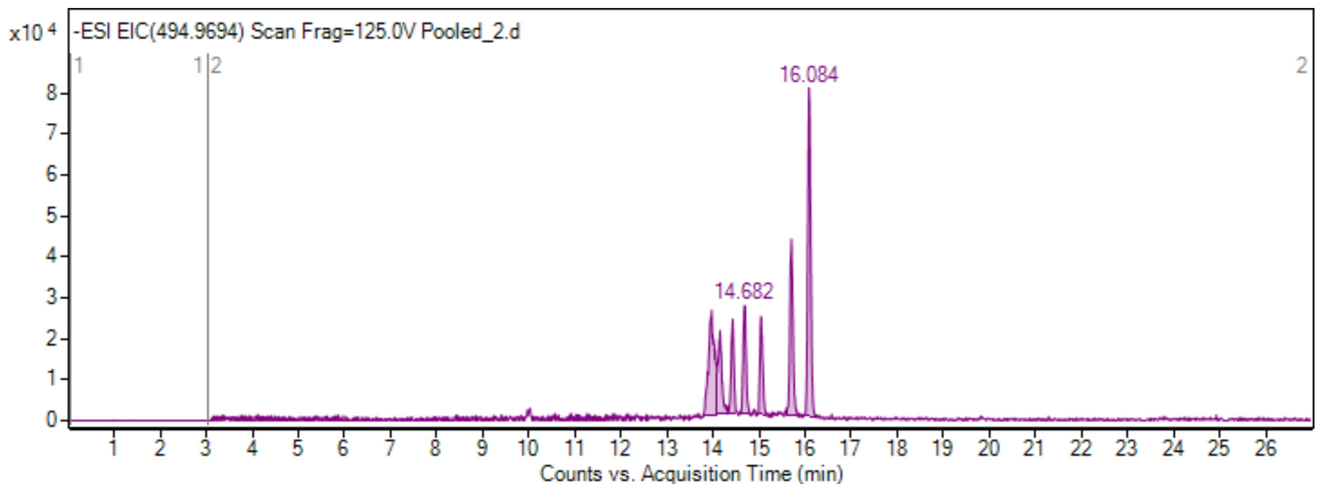


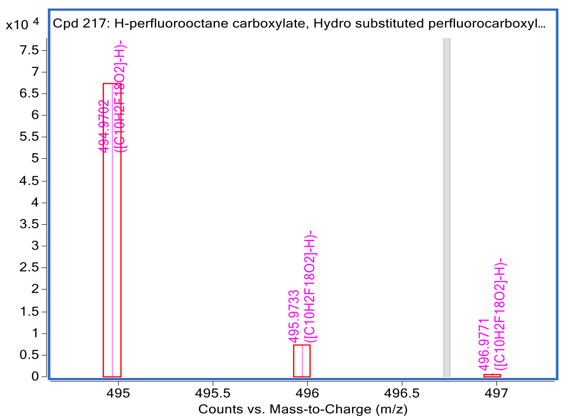
CE = 40V

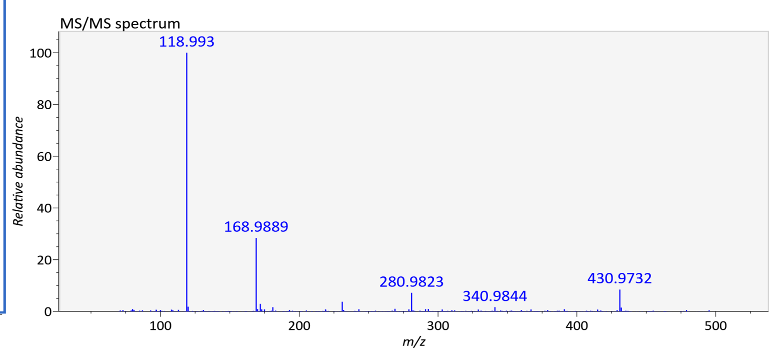
MS/MS ion (m/z)	Molecular formula	Match
118.9932	$C_2F_5^-$	Fluoromatch Library
292.9828	$C_7F_{11}^-$	-
442.9734	$C_{10}F_{17}^-$	Fluoromatch Library

Compound 20: H-substituted-PFCA (n=8)





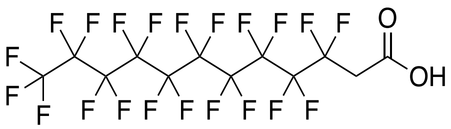


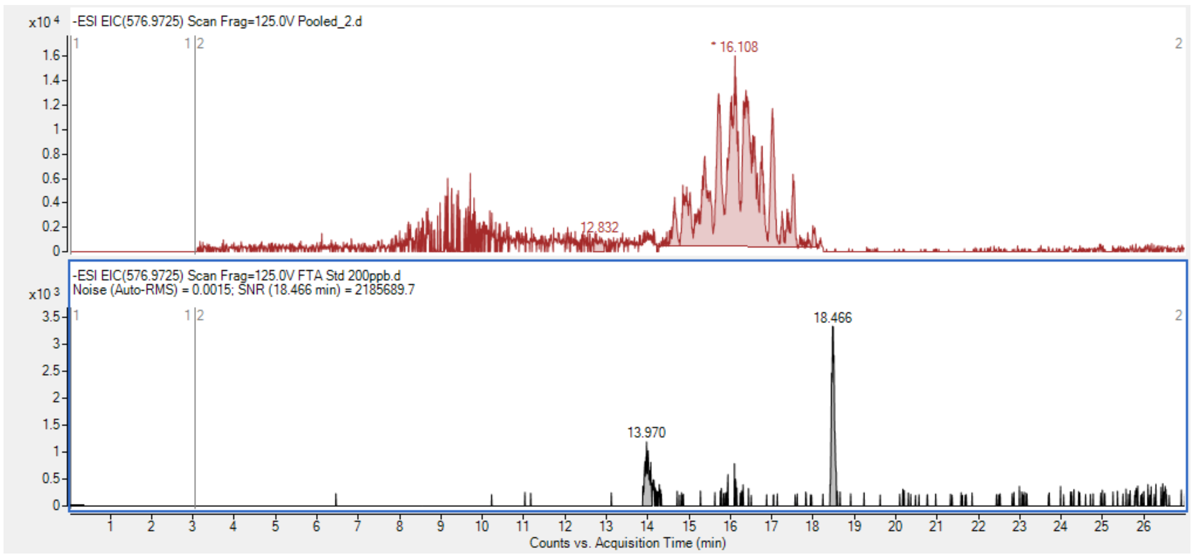


CE = 40V

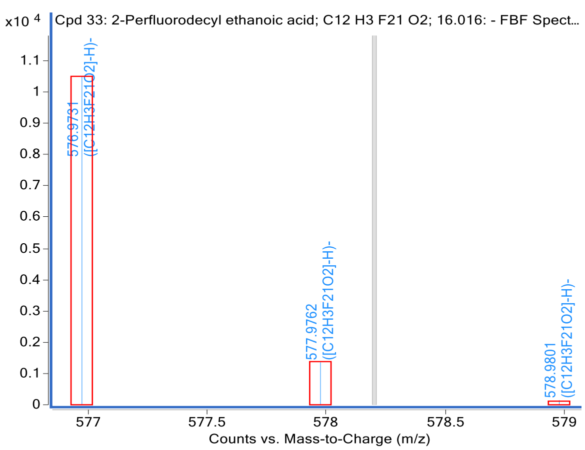
MS/MS ion (m/z)	Molecular formula	Match
118.9932	$C_2F_5^-$	Fluoromatch Library
168.9889	$C_3F_7^-$	Fluoromatch Library
430.9732	$C_9F_{17}^-$	Fluoromatch Library

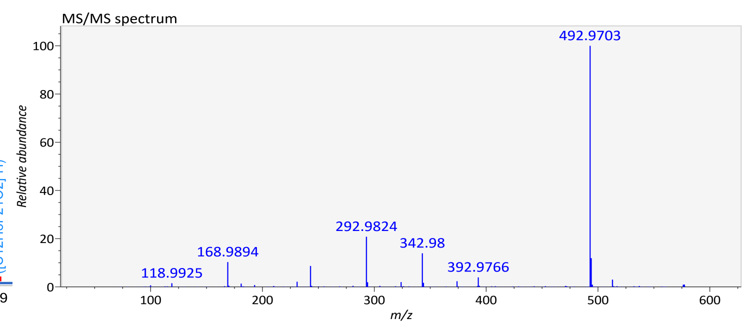
Compound 21: 10:1 FT carboxylic acid





Top: Pooled sample Bottom: Linear standard 2-perfluorodecyl ethanoic acid (10:2 FTCA):

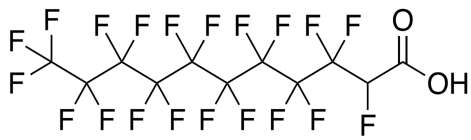


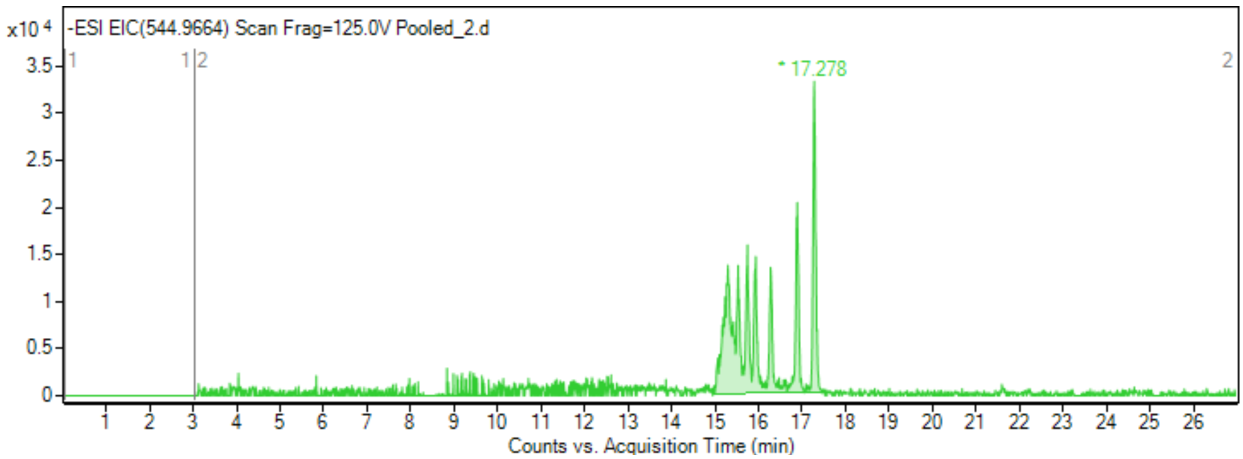


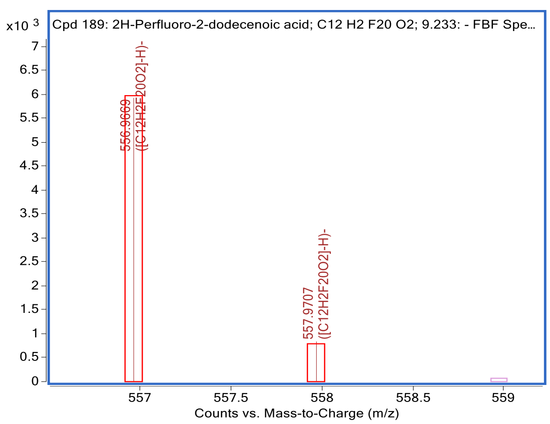
CE = in source and 40V

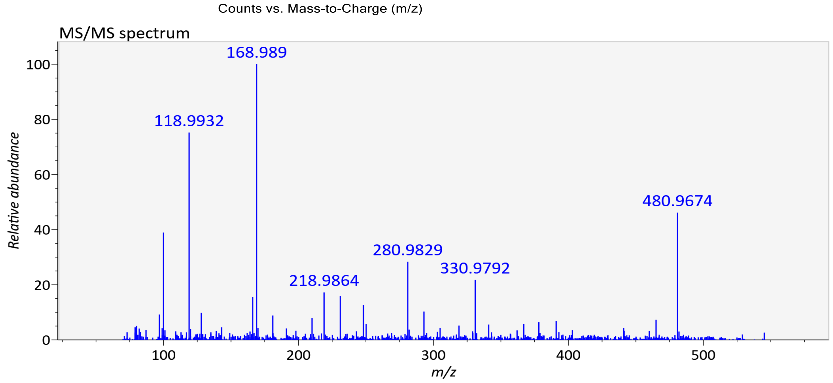
MS/MS ion (m/z)	Molecular formula	Match
118.9932	$C_2F_5^-$	Standard
292.9828	$C_7F_{11}^-$	Standard
492.9703 (in source)	$C_{11}F_{19}^-$	Standard

Compound 22: H-substituted-PFCA (n=9)





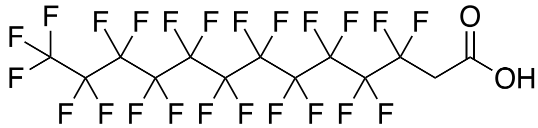


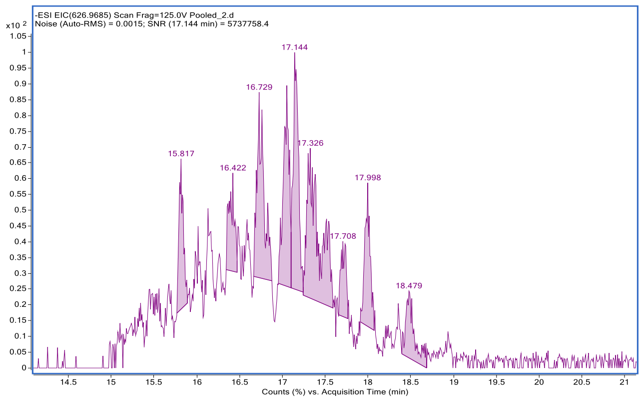


CE = 40V

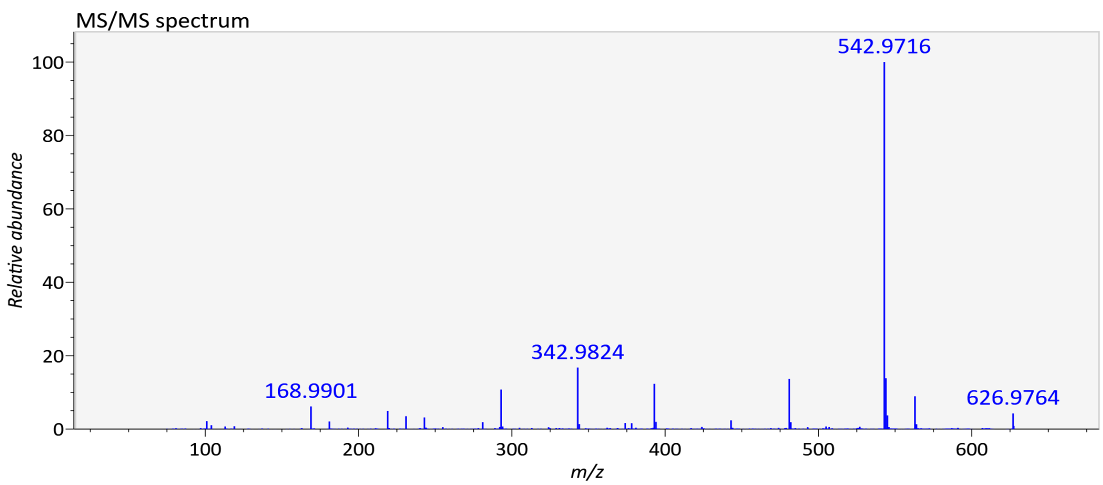
MS/MS ion (m/z)	Molecular formula	Match
118.9932	$C_2F_5^-$	Fluoromatch Library
168.9889	$C_3F_7^-$	Fluoromatch Library
480.9674	$C_{10}F_{19}^-$	-

Compound 23: 11:1 FT carboxylic acid





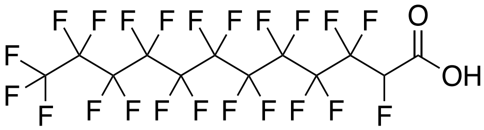
Abundance too low for accurate isotopic profile

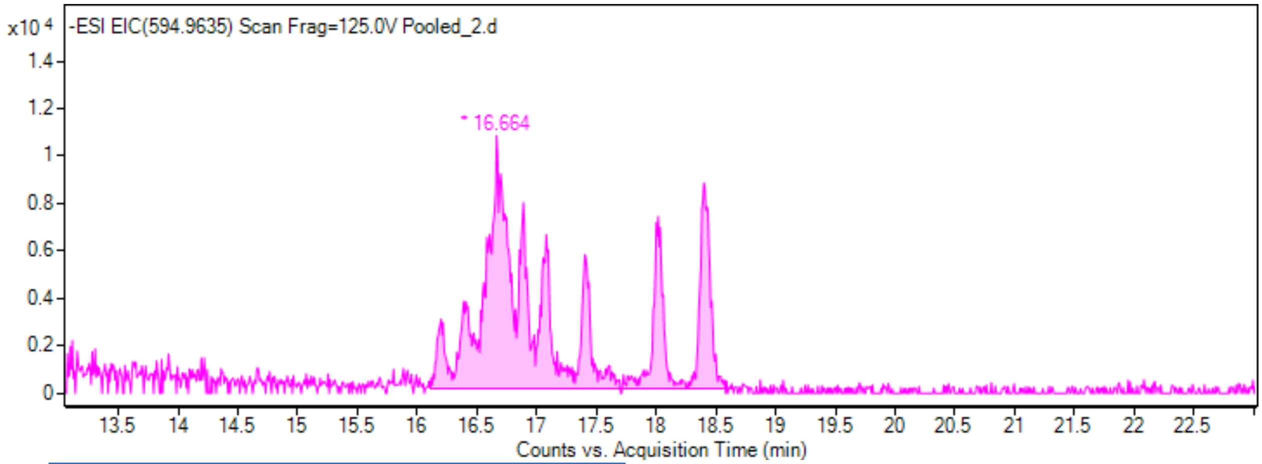


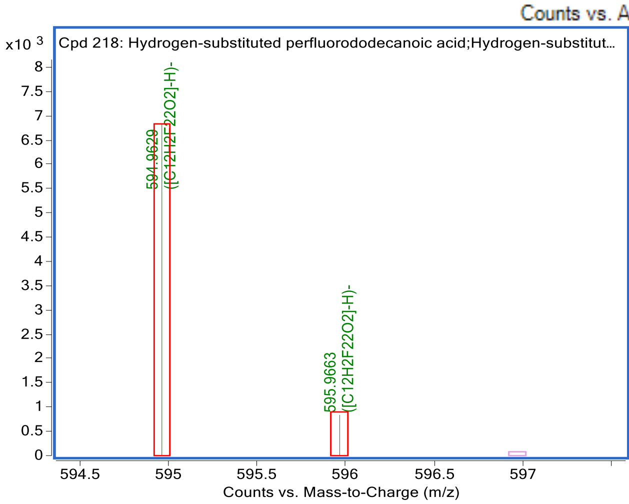
CE = 40V

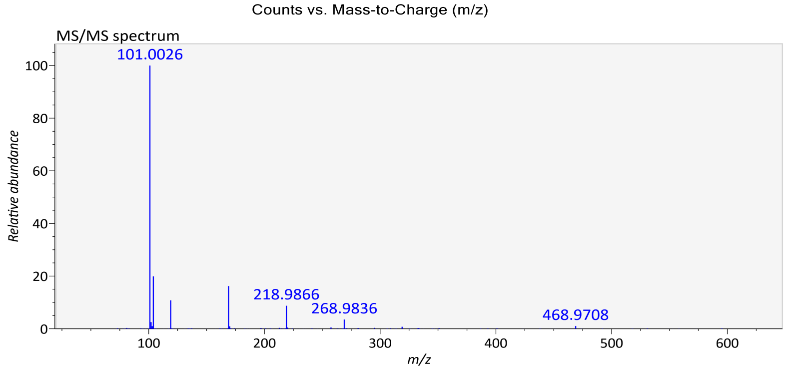
MS/MS ion (m/z)	Molecular formula	Match
242.9880	$C_6F_9^-$	Fluoromatch Library
342.9824	$C_8F_{13}^-$	Fluoromatch Library
542.9716	$C_{12}F_{21}^-$	Fluoromatch Library

Compound 24: H-substituted-PFCA (n=10)









CE = 40V

MS/MS ion (m/z)	Molecular formula	Match
118.9928	$C_2F_5^-$	Fluoromatch Library
168.9895	$C_3F_7^-$	Fluoromatch Library
268.9836	$C_5F_{11}^-$	Fluoromatch Library

Appendix B: Air Mass Back Trajectories

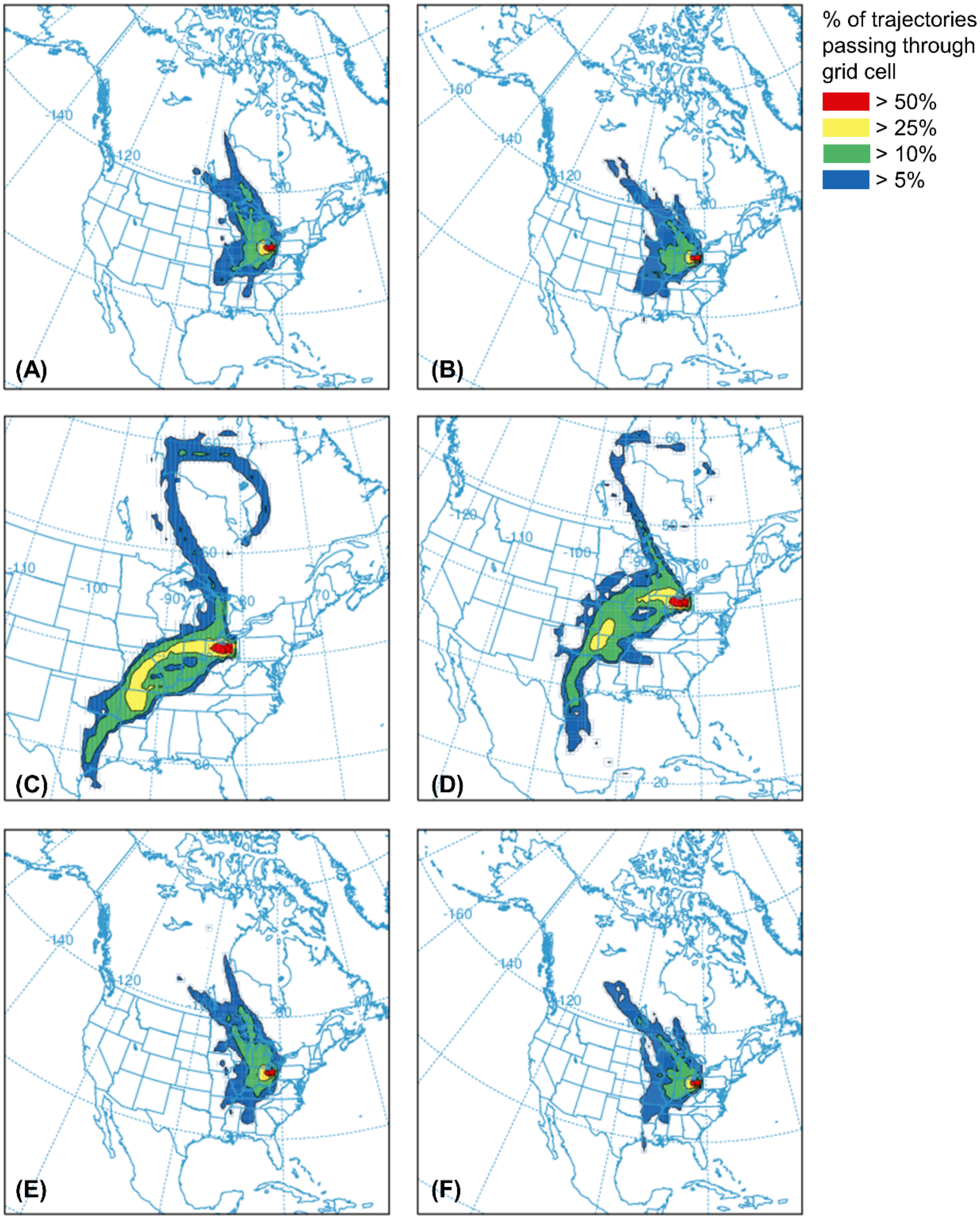


Figure B1. Frequency plots of air mass back trajectories at Ashland, OH for (A-B) all precipitation events (*n* = 10); (C-D) precipitation events with Σ_{PFAS} > 50% of the maximum deposition flux (4 July 2019); and (E-F) precipitation events with $\Sigma_{PFAS} \leq$ 50% of the maximum deposition flux (*n* = 9). The altitude is 500 m above ground level for panels A/C/E and 1000 m above ground level for panels B/D/F. The color scheme indicates the fraction of trajectories crossing a grid cell: >50% for red, >25% for yellow, >10% for green, and >5% for blue. See the methods section of the main text for additional HYSPLIT parameters.

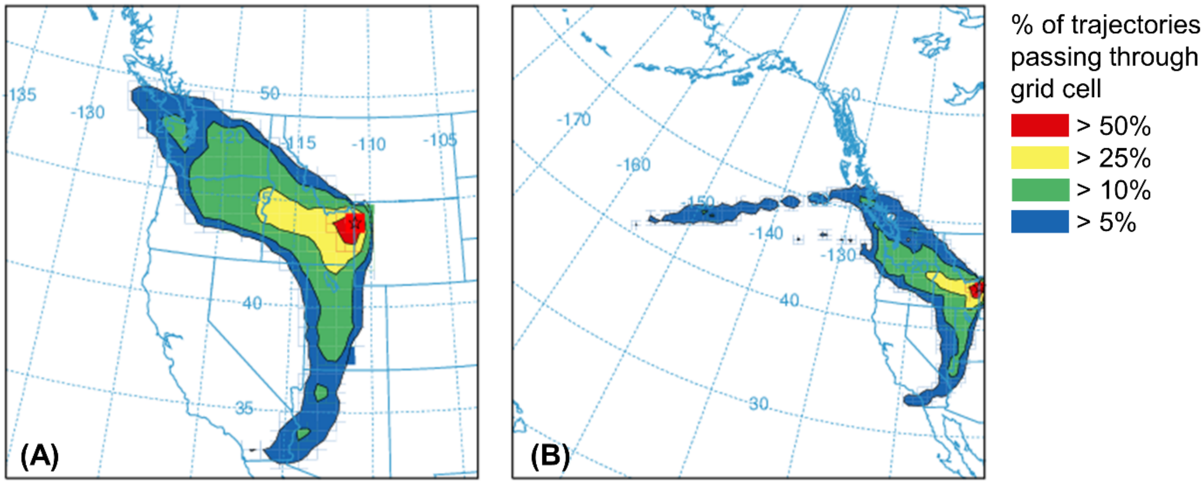


Figure B2. Frequency plots of air mass back trajectories at Jackson Hole, WY for all precipitation events (n = 3) at an altitude of 500 m above ground level (A) and 1000 m above ground level (B). The color scheme indicates the fraction of trajectories crossing a grid cell: >50% for red, >25% for yellow, >10% for green, and >5% for blue. See the methods section of the main text for additional HYSPLIT parameters.

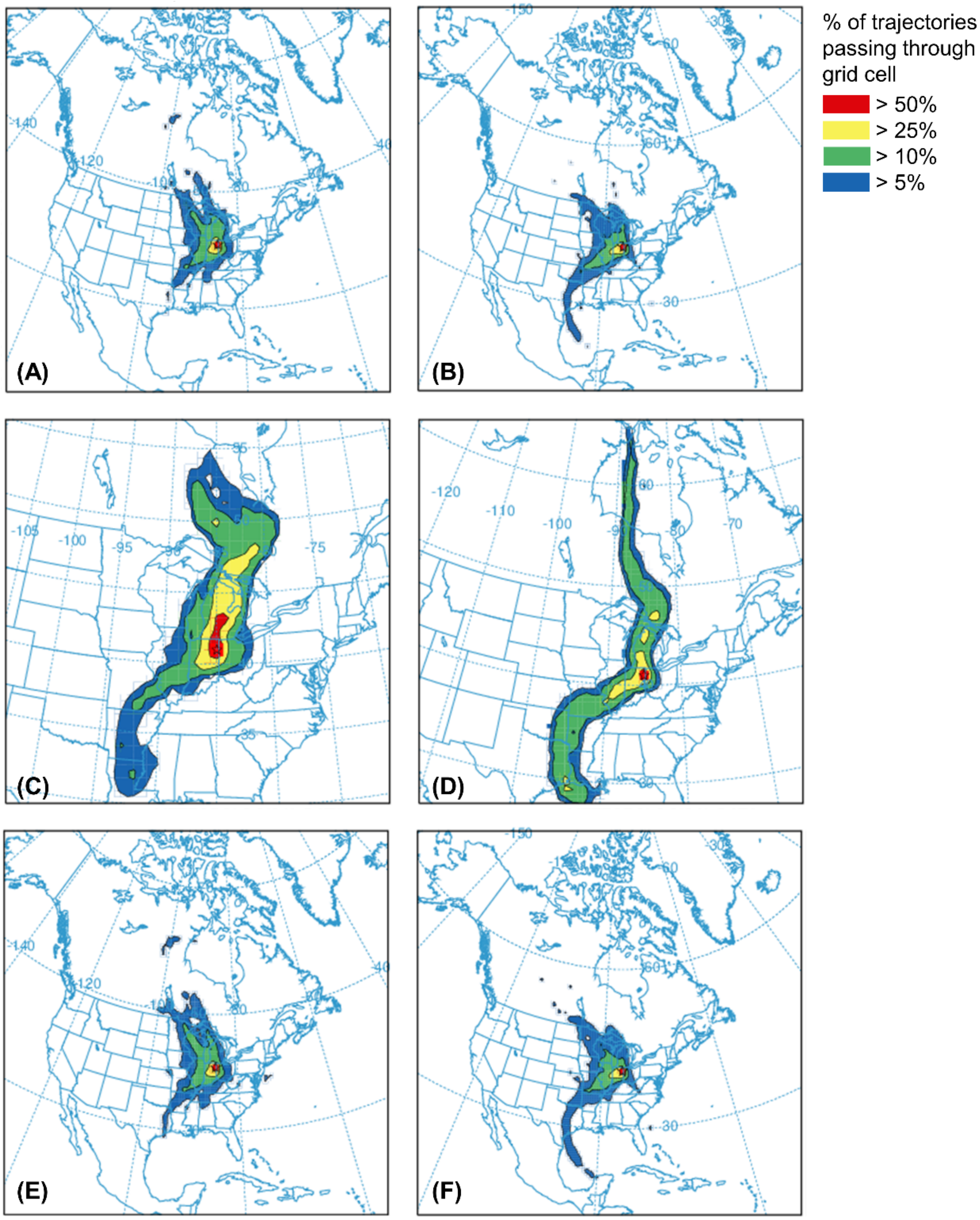


Figure B3. Frequency plots of air mass back trajectories at Rockford, OH for (A-B) all precipitation events (n = 8); (C-D) precipitation events with Σ_{PFAS} > 50% of the maximum deposition flux (23 June 2019); and (E-F) precipitation events with $\Sigma_{PFAS} \leq$ 50% of the maximum deposition flux (n = 7). The altitude is 500 m above ground level for panels A/C/E and 1000 m above ground level for panels B/D/F. The color scheme indicates the fraction of trajectories crossing a grid cell: >50% for red, >25% for yellow, >10% for green, and >5% for blue. See the methods section of the main text for additional HYSPLIT parameters.

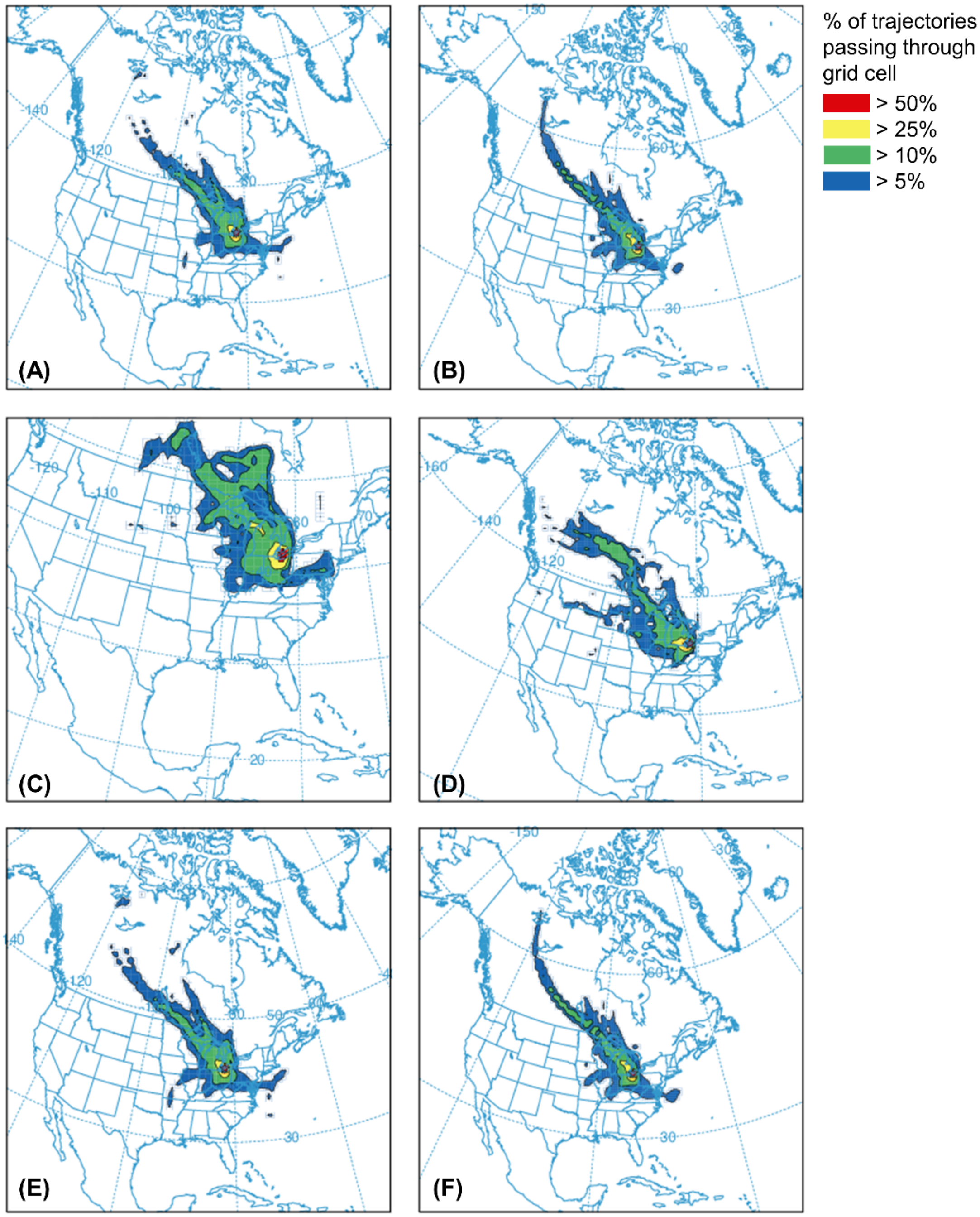


Figure B4. Frequency plots of air mass back trajectories at Shaker Heights, OH for (A-B) all precipitation events (n = 10); (C-D) precipitation events with Σ_{PFAS} > 50% of the maximum deposition flux (16 July 2019); and (E-F) precipitation events with $\Sigma_{PFAS} \leq$ 50% of the maximum deposition flux (n = 9). The altitude is 500 m above ground level for panels A/C/E and 1000 m above ground level for panels B/D/F. The color scheme indicates the fraction of trajectories crossing a grid cell: >50% for red, >25% for yellow, >10% for green, and >5% for blue. See the methods section of the main text for additional HYSPLIT parameters.

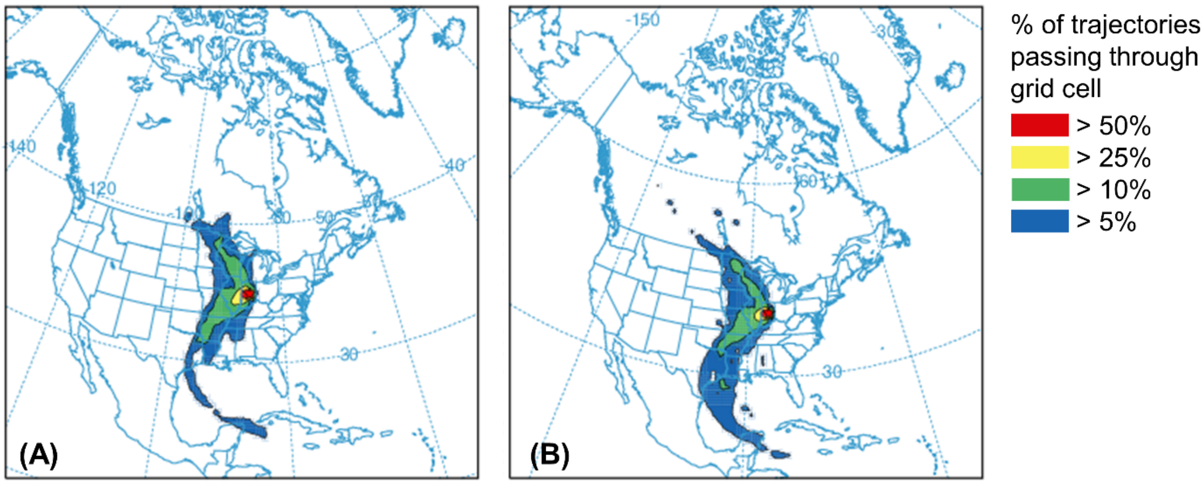


Figure B5. Frequency plots of air mass back trajectories at Whitestown, IN for all precipitation events (n = 5) at an altitude of 500 m above ground level (A) and 1000 m above ground level (B). The color scheme indicates the fraction of trajectories crossing a grid cell: >50% for red, >25% for yellow, >10% for green, and >5% for blue. See the methods section of the main text for additional HYSPLIT parameters.

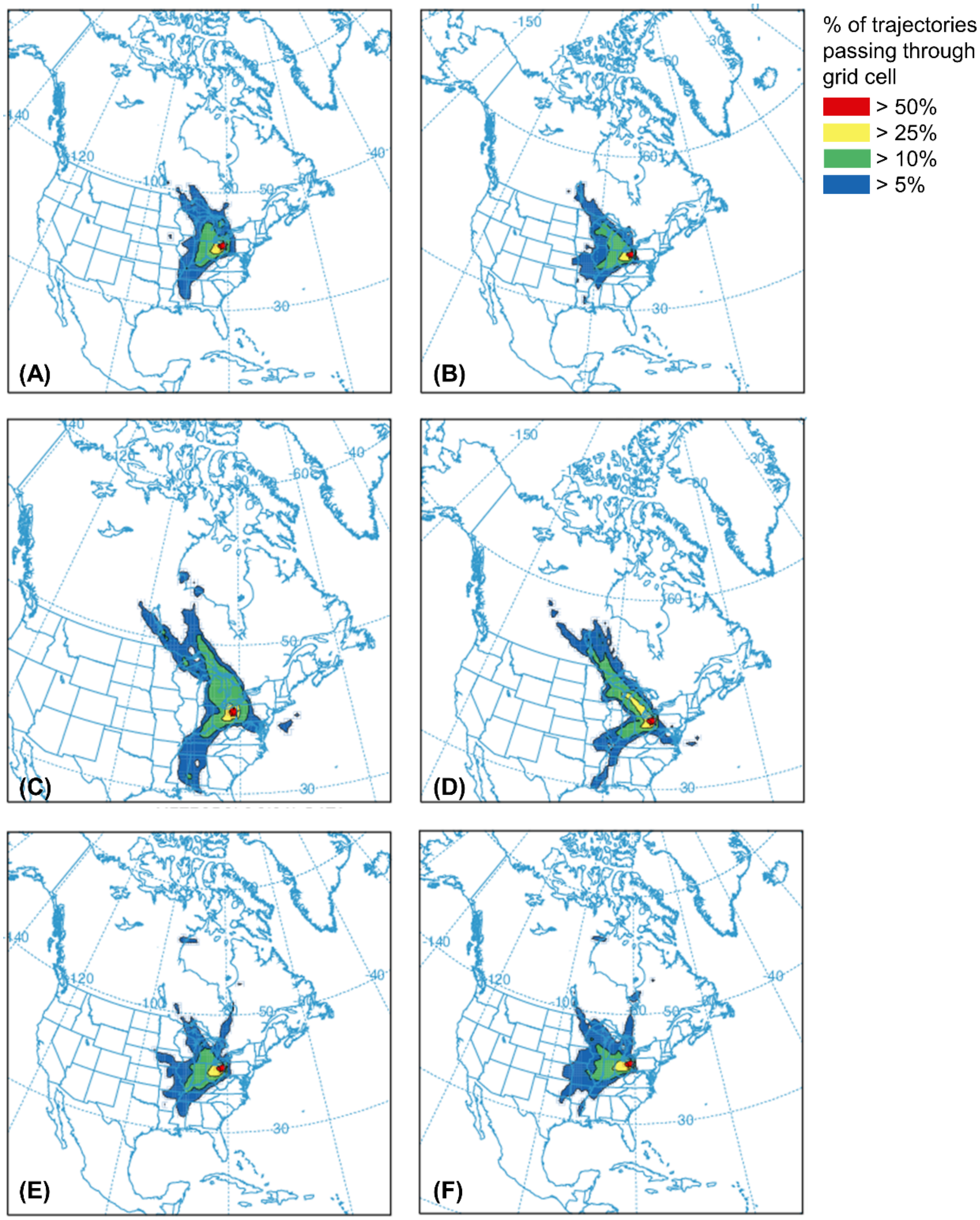


Figure B6. Frequency plots of air mass back trajectories at Willoughby, OH for (A-B) all precipitation events (n = 10); (C-D) precipitation events with Σ_{PFAS} > 50% of the maximum deposition flux (13 June, 20 June, 6 Aug, and 7 Aug 2019); and (E-F) precipitation events with $\Sigma_{PFAS} \leq$ 50% of the maximum deposition flux (n = 6). The altitude is 500 m above ground level for panels A/C/E and 1000 m above ground level for panels B/D/F. The color scheme indicates the fraction of trajectories crossing a grid cell: >50% for red, >25% for yellow, >10% for green, and >5% for blue. See the methods section of the main text for additional HYSPLIT parameters.

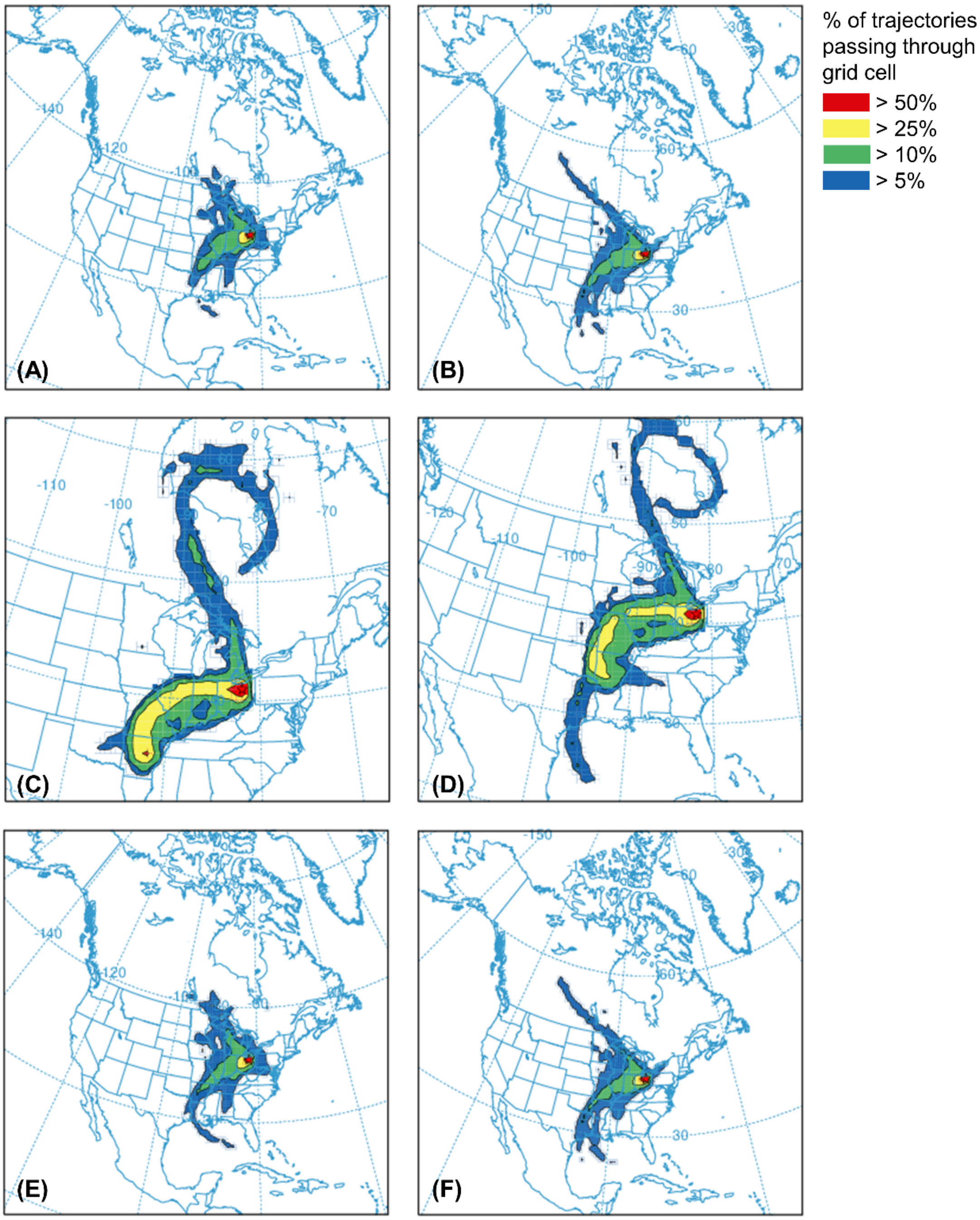


Figure B7. Frequency plots of air mass back trajectories at Wooster, OH for (A-B) all precipitation events (n = 10); (C-D) precipitation events with Σ_{PFAS} > 50% of the maximum deposition flux (6 July 2019); and (E-F) precipitation events with $\Sigma_{PFAS} \leq$ 50% of the maximum deposition flux (n = 9). The altitude is 500 m above ground level for panels A/C/E and 1000 m above ground level for panels B/D/F. The color scheme indicates the fraction of trajectories crossing a grid cell: >50% for red, >25% for yellow, >10% for green, and >5% for blue. See the methods section of the main text for additional HYSPLIT parameters.

References

1 K. A. Pike, P. L. Edmiston, J. J. Morrison and J. A. Faust, Correlation Analysis of Perfluoroalkyl Substances in Regional U.S. Precipitation Events, *Water Res.*, 2021, **190**, 116685.

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