Non-target Discovery of Per- and Polyfluoroalkyl Substances in Atmospheric Particulate Matter and Gaseous Phase Using Cryogenic Air Sampler

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Section 1. Chemicals and Reagents.

Formic acid (HPLC grade, purity: 99%) and ammonium hydroxide solution ~25% (HPLC grade) was purchased from ROE SCIENTIFIC ING (USA). Ammonium acetate (HPLC grade) was purchased from CNW technologies GmbH (Duesseldorf, Germany). Water (LCMS, purity> 99.99%)was purchased from Fisher (USA). Methanol (HPLC grade, purity: 99.9%) was purchased from Merck (Germany). The detail information of standards is shown in **Table S1**.

Table S1. The compound name, abbreviations, molecular formula, supplier and purity of standards.

Compound name	Abbreviation	Molecular formula	Supplier	Purity
Perfluorobutane sulfonate	PFBS	C4HF9O3S	Woke	98%
Perfluorohexane sulfonate	PFHxS	C6HF13O3S	Sigma-Aldrich	98%
n-perfluoro-1-octanesulfonate	PFOS	C8HF17O3S	Wellington Laboratories	98%
Perfluoropentanoate	PFPeA	C5HF9O2	Sigma-Aldrich	97%
Perfluorohexanoate	PFHxA	C6HF11O2	Sigma-Aldrich	97%
Perfluoroheptanoate	PFHpA	C7HF13O2	Sigma-Aldrich	99%
Perfluorooctanoate	PFOA	C8HF15O2	Alfa Aesar	95%
Perfluorononanoate	PFNA	C9HF17O2	Alfa Aesar	97%
Perfluorodecanoate	PFDA	C10HF19O2	Sigma-Aldrich	98%
Perfluoroundecanoate	PFUnDA	C11HF21O2	Sigma-Aldrich	95%
Perfluorododecanoate	PFDoDA	C12HF23O2	Sigma-Aldrich	95%
Perfluorotridecanoate	PFTrDA	C13HF25O2	Sigma-Aldrich	97%
Perfluorotetradecanoate	PFTeDA	C14HF27O2	Sigma-Aldrich	97%
2-(6-Chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexoxy)-1,1,2,2-tetrafluoroethanesulfonic acid	6:2 Cl-PFESA	C8HClF16O4S	Wellington Laboratories	98%
3,3,4,4,5,5,6,6,7,7,8,8,8-tidecafluorooctanesulphonic acid	6:2 FTS	C8H5F13O3S	Wellington Laboratories	98%
2-perfluorooctyl ethanoic acid	8:2 FTA	C10H3F17O2	Wellington Laboratories	98%
2-perfluorodecyl ethanoic acid	10:2 FTA	C12H3F21O2	Wellington Laboratories	98%
2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptanoic acid	7-H-PFHpA	C7H2F12O2	Fluorochem	98%

Section 2. Sample Preparation.

Sample preparation of quartz fiber filter containing atmospheric particulate matter used our method previous study.[1] Each filter sample was placed into a 15mL polypropylene centrifuge tube separately. Each sample will be subjected to four cycles of 10 minutes ultrasonic extractions in a 40 °C water bath with 5mL, 5mL, 5mL and 3mL of methanol, respectively. The samples were centrifuged at 5000 rpm for five minutes after each cycle of ultrasonic extraction and the four extracted supernatants for one sample were combined in a 15mL polypropylene centrifuge tube.

Liquid samples collected by CMS were enriched through the sample preparation method in our previous study of water samples.[2] Each sample was enriched by solid phase extraction (SPE) using Oasis MAX cartridge (6 cc, 500 mg, Waters, Ireland), Oasis MCX cartridge (6 cc, 500 mg, Waters, Ireland) and Oasis HLB cartridge (6 cc, 500 mg, Waters, Ireland) sequentially. Precondition and elution solution for each cartridge are listed in **Table S2**. The eluent is collected in a 15mL polypropylene centrifuge tube for concentration under nitrogen and the eluents of the three cartridges for the same sample were combined in one 15mL polypropylene centrifuge tube.

All the ultrasonic extract and SPE eluent were reduced to a volume of 1 mL by evaporation under a gentle stream of nitrogen. The final concentrated extract was passed through a polypropylene-membrane syringe filter (Acrodisc GHP, 13 mm, 0.2 μm, Waters) and transferred into a polypropylene vial for instrumental analysis.

Table S2. The Specification, precondition and elution solution of SPE cartridges.

SPE cartridge	Specification	Precondition solution	Elution solution
Oasis MAX	6 cc, 500 mg	10mL 2% NH4OH in methanol 10mL methanol 10mL water	10mL 2% HCOOH in methanol
Oasis MCX	6 cc, 500 mg	10mL 2% HCOOH in methanol 10mL methanol 10mL water	10mL 2% NH4OH in methanol
Oasis HLB	6 cc, 500 mg	10mL n-hexane 10mL dichloromethane 10mL methanol 10mL water	10 mL methanol

Section 3. UPLC-HRMS Analysis.

UPLC-HRMS Analysis for non-target screening was performed on ultra-performance liquid chromatography (UPLC; UltiMate 3000 Series, Thermo Fisher Scientific, Bremen, Germany) coupled with a high-resolution orbitrap mass spectrometer (Q Exactive Focus, Thermo Fisher Scientific, Bremen, Germany) with an electrospray ionization (ESI) source operating in negative ion mode. Sample separation used a C18 column (ACQUITY UPLC BEH C18, 1.7μm, 2.1×150mm, Waters, Ireland) kept at 40 °C. The mobile phases used were A: 2 mmol ammonium acetate, 5% methanol in water and B: methanol with the flow rate of 0.3 L/min. Mobile phase gradient elution conditions are shown in **Table S3**. The injection volume was 10 μL. The parameters of the ion source were: spray voltage, 2500 V; capillary temperature, 320 °C; sheath gas, 48; aux gas, 11; spare gas, 2. The Q Exactive Focus was operated in Full MS combined with Discovery mode data dependent MS/MS (dd MS^2). The resolution of Full MS is 70000 with the mass range of m/z 80 to 1000 and the resolution of dd MS^2 is 17500 with fixed first mass of 50 m/z. The other parameters were: nce, 20, 35, 50; AGC target, 5e4; loop count, 3.

Table S3. Mobile phase gradient elution condition.

Time / min	% A (2 mmol ammonium acetate 5% methanol in water)	% B (methanol)
0	100	0
1	100	0
9	75	25
18	50	50
28	25	75
39	0	100
48	0	100
48.1	100	0
55	100	0

Table S4. The procedural recovery (20 μg L^{-1}) and the sensitivity of UPLC-HRMS analysis with known PFASs standards.

Analyte	Theoretical mass / Da	1 μg L^{-1}				5 μg L^{-1}				Procedural recovery (n=3) / Mean(S.D.)	
		RT / min	Experimental mass / Da	Error / mDa	Error / ppm	RT / min	Experimental mass / Da	Error / mDa	Error / ppm	Particulate Matter	Gaseous Phase
PFBS	298.94299	17.22	298.94312	0.13	0.43	17.12	298.94305	0.06	0.20	102.1%(0.03)	116.4%(0.01)
PFHxS	398.93660	23.87	398.93661	0.01	0.03	23.78	398.93658	-0.02	-0.05	101.3%(0.07)	90.4%(0.04)
PFOS	498.93022	27.83	498.93036	0.14	0.28	27.75	498.93030	0.08	0.16	103.1%(0.04)	94.5%(0.20)
PFPeA	262.97601	15.47	262.97620	0.19	0.72	15.41	262.97614	0.13	0.49	104.3%(0.06)	94.9%(0.02)
PFHxA	312.97281	20.29	312.97308	0.27	0.86	20.29	312.97296	0.15	0.48	85.6%(0.14)	94.5%(0.06)
PFHpA	362.96962	23.49	362.96985	0.23	0.63	23.41	362.96991	0.29	0.80	101.9%(0.06)	102.4%(0.06)
PFOA	412.96643	25.85	412.96671	0.28	0.68	25.78	412.96655	0.12	0.29	102.8%(0.05)	100.2%(0.10)
PFNA	462.96323	27.73	462.96375	0.52	1.12	27.67	462.96338	0.15	0.32	102.7%(0.04)	102.4%(0.07)
PFDA	512.96004	29.29	512.96002	-0.02	-0.04	29.24	512.95990	-0.14	-0.27	107.1%(0.03)	100.1%(0.18)
PFUnDA	562.95685	30.58	562.95721	0.36	0.64	30.56	562.95709	0.24	0.43	110.1%(0.05)	99.5%(0.29)
PFDoDA	612.95365	31.77	612.95428	0.63	1.03	31.72	612.95404	0.39	0.64	135.9%(0.09)	80.1%(0.10)
PFTrDA	662.95046	32.78	662.95087	0.41	0.62	32.72	662.95099	0.53	0.80	139.7%(0.11)	74.5%(0.04)
PFTeDA	712.94726	33.66	712.94812	0.86	1.21	33.61	712.94781	0.55	0.77	111.1%(0.36)	49.8%(0.02)

Section 4. Non-target Screening and Identification of PFASs.

The peak picking process of raw data is implemented by Compound Discoverer 3.0 (Thermo Fisher Scientific). The workflow composed of Input Files, Select Spectra, Align Retention Time, Detect Compounds, Group Compounds and Assign Compound Annotations, successively. Detailed parameters are Mass Tolerance 5 ppm, Maximum Shift 2 min, Intensity Tolerance 30%, S/N threshold 3, Min. Peak Intensity 10000, Max. Peak Width 0.5 min, Min. # Scans per Peak 5, Min. # Isotopes 2 and RT Tolerance 0.2 min.

PFASs homologues were found from peaks picked above using MATLAB script for PFAS Homologue Analysis described in our previous studies.[1] In this script, the input data was the peak list including exact mass and retention time, and the output result was the homologue candidate list. The mass difference of any two peaks was calculated during the running of script. The PFASs homologues were identified by the mass difference of 49.99681 Da (CF2, mass error < 5ppm) among the exact mass of peaks.

The PFASs homologues were screened by database firstly for identification. The database includes the laboratory's existing standards, the PFASs we have identified in previous studies[1, 2] and the PFASs with MS/MS spectrum information in the Norman database[3]. The database screening was using TraceFinder 4.1 General Quan (Thermo Fisher Scientific). PFASs information data including name, parent ion and product ion was imported into TraceFinder as Compound Database by CSV format. A target

screening method was used to screen the PFASs in created Compound Database with Mass Precision 5, S/N Ratio Threshold 3 and Mass Tolerance 5 ppm for Peaks, Intensity Threshold 1000 and Mass Tolerance 5 ppm for Fragment Ions.

For the PFASs homologues that not matched database, molecular formula and MS/MS fragments were calculated by Compound Discoverer 3.0 (function Predict Compositions) and Qual Browser (Thermo Fisher Scientific). The elements setting included C (3-50), H (0-50), F (0-50), O (0-8), N (0-4), P (0-4), S (0-4), Cl (0-2). The mass tolerance was 5 ppm for parent ion and 5 mDa for fragments.

With Sirius and CSI:FingerID, the relationship of fragmentation and the formula of fragments were predicted based on the MS/MS spectra, which could assist identification of structure. The confidence of the identification results is based on previous study.[4] Briefly, Level 1: confirmed structure by reference standard; Level 2a: probable structure matching literature or library spectrum data; Level 2b: probable structure with diagnostic evidence but no standard or literature information is available for confirmation; Level 3: tentative candidate(s) with evidence existing for possible structure(s), but insufficient information for one exact structure only; Level 4: unequivocal molecular formula and Level 5: exact mass.

Table S5. The identified PFASs with level 4 or above. The numbers in the "Particulate Matter" and "Gaseous Phase" show the distribution ratio in each phase and were converted by chromatographic peak area.

Class	Serial Number	Formula	Level	Theoretical Molecular Weight	Mass Error /ppm	RT /min	RT delta /min	Particulate Matter				Gaseous Phase
								> 10μm	10-2.5μm	2.5-1μm	< 1μm	
Class 1	A01	C4HF7O2	2	213.98648	0.30~2.42	9.06		0.40	0.31		0.29	
PFCAs	A02	C5HF9O2	1	263.98328	0.01~0.82	15.08	0.09~0.27				0.48	0.52
	A03	C6HF11O2	1	313.98009	0.38~2.53	19.82	0.00~0.22	0.06	0.08		0.70	0.16
	A04	C7HF13O2	1	363.97690	0.04~2.40	22.88	0.09~0.15	0.11	0.09	0.07	0.67	0.06
	A05	C8HF15O2	1	413.97370	0.29~1.78	25.31	0.02~0.15	0.05	0.18	0.17	0.50	0.11
	A06	C9HF17O2	1	463.97051	0.26~1.51	27.22	0.00~0.05	0.29	0.12	0.19	0.10	0.31
	A07	C10HF19O2	1	513.96732	0.04~0.08	28.83	0.03~0.06	0.26		0.23		0.51
	A08	C12HF23O2	1	613.96093	1.03~1.24	31.35	0.03~0.06	0.61				0.39
Class 2	B01	C6HF13O3S	1	399.94388	0.80~1.77	23.28	0.11~0.19	0.06	0.58	0.18	0.18	
PFSAs	B02	C8HF17O3S	1	499.93749	0.09~2.39	27.30	0.08~0.20		0.33	0.67		
Class 3 n:2 FTSs	C01	C8H5F13O3S	1	427.97518	0.05~1.35	25.18	0.06~0.22		0.96	0.04		
Class 4 Cl-PFESAs	D01	C8HClF16O4S	1	531.90286	0.8~1.29	29.29	0.11~0.16	0.03	0.41	0.42	0.14	
Class 5	E01	C16H9F26O4P	2	789.98233	0.44	33.04		1.00				
diPAPs	E02	C18H9F30O4P	2	889.97594	4.35	34.37		1.00				
Class 6 H-PFCAs	F01	C7H2F12O2	3	345.98632	0.42~1.84	18.60		0.10	0.20	0.09	0.57	0.04
	F02	C8H2F14O2	3	395.98312	0.18~1.83	21.42		0.13	0.32	0.08	0.45	0.02
	F03	C9H2F16O2	3	445.97993	0.76~1.93	23.72		0.15	0.37	0.12	0.36	0.01

Class	Serial Number	Formula	Level	Theoretical Molecular Weight	Mass Error /ppm	RT /min	RT delta /min	Particulate Matter				Gaseous Phase
								> 10μm	10-2.5μm	2.5-1μm	< 1μm	
	F04	C10H2F18O2	3	495.97674	0.22~1.83	25.65			0.75		0.25	
	F05	C11H2F20O2	3	545.97354	0.51~1.88	27.30		0.06	0.53	0.17	0.24	
	F06	C12H2F22O2	3	595.97035	0.52~1.75	28.72		0.11	0.41	0.23	0.25	0.0003
	F07	C13H2F24O2	3	645.96716	0.79~2.49	29.93		0.09	0.45	0.26	0.20	
	F08	C14H2F26O2	3	695.96396	0.46~1.91	30.98		0.08	0.43	0.30	0.19	
	F09	C15H2F28O2	3	745.96077	0.98~1.80	31.92		0.10	0.46	0.29	0.14	0.0004
	F10	C16H2F30O2	3	795.95758	0.79~2.74	32.76		0.09	0.48	0.33	0.10	
	F11	C17H2F32O2	3	845.95438	0.09~3.20	33.51		0.11	0.43	0.33	0.13	0.002
	F12	C19H2F36O2	3	945.94799	0.79~1.90	34.81		0.10	0.46	0.33	0.11	
Class 7	G01	C7HClF14O3	3	433.93907	0.00~1.56	28.31		0.42	0.45			0.13
Cl-PFDEA	G02	C8HClF16O3	3	483.93587	0.23~1.51	29.49		0.24	0.44	0.03		0.29
	G03	C9HClF18O3	3	533.93268	0.04~0.15	30.51		0.29	0.25	0.22	0.24	
	G04	C10HClF20O3	3	583.92949	0.26~2.35	31.18		0.21				0.79
	G05	C11HClF22O3	3	633.92629	0.32~0.36	32.02		0.50	0.50			
Class 8	H01	C9HClF18O4	3	549.92759	0.05~2.07	30.72			0.31			0.69
Cl-PFTrEA	H02	C10HClF20O4	3	599.92440	0.02~0.90	31.46					0.26	0.74
	H03	C11HClF22O4	3	649.92121	0.02~0.59	32.22		0.52	0.18	0.13	0.16	
	H04	C12HClF24O4	3	699.91801	0.14~0.49	32.95		0.29	0.23	0.26	0.21	
Class 9	I01	C11HClF22O5	3	665.91612	0.23~0.32	32.46		0.14	0.15	0.14	0.15	0.42
Cl-PFTeEA	I02	C12HClF24O5	3	715.91293	0.15~2.63	33.11		0.28	0.34	0.25	0.13	
Class 10	J01	C12HCl2F21O6	3	709.88149	0.25~1.28	31.72		0.80			0.20	
2Cl-PFTeECA	J02	C13HCl2F23O6	3	759.87829	0.26~0.42	32.49		0.31	0.23	0.24	0.21	

Class	Serial Number	Formula	Level	Theoretical Molecular Weight	Mass Error /ppm	RT /min	RT delta /min	Particulate Matter				Gaseous Phase
								> 10μm	10-2.5μm	2.5-1μm	< 1μm	
Class 11	K01	C13H2ClF23O6	4	725.91727	0.11~1.28	30.51		0.55	0.45			
H,Cl-PFTeECA	K02	C16H2ClF29O6	4	875.90768	0.26~0.42	32.98		0.24	0.20	0.42	0.14	
Class 12	L01	C5H3F7O2	4	228.00213	1.24~2.86	12.00		0.002	0.03	0.43	0.53	
n:2 FTAs	L02	C8H3F13O2	4	377.99255	0.00~1.59	23.50						1.00
	L03	C10H3F17O2	1	477.98616	1.34~4.15	23.77	0.28~0.34	0.10	0.28	0.06	0.48	0.07
	L04	C12H3F21O2	1	577.97977	0.14	27.91	0.16		1.00			
Class 13	M01	C4HF7O3	4	229.98139	4.89	6.82			1.00			
1:n PFECAs	M02	C5HF9O3	4	279.97820	0.10~1.22	11.83						1.00
	M03	C15HF29O3	4	779.94626	0.92	29.01		1.00				

Table S6. The CAS number, IUPAC name and SMILE for the identified PFASs with level 1 and level 2.

Class	Formula	Level	CAS Number	IUPAC Name	SMILE
Class 1 PFCAs	C4HF7O2	2	375-22-4	2,2,3,3,4,4,4-heptafluorobutanoate	C(=O)(C(C(C(F)(F)F)(F)F)(F)F)O
	C5HF9O2	1	2706-90-3	2,2,3,3,4,4,5,5,5-nonafluoropentanoate	C(=O)(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)O
	C6HF11O2	1	307-24-4	2,2,3,3,4,4,5,5,6,6,6-undecafluorohexanoic acid	C(=O)(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)O
	C7HF13O2	1	375-85-9	2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptanoate	C(=O)(C(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)O
	C8HF15O2	1	335-67-1	2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoic acid	C(=O)(C(C(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)O
	C9HF17O2	1	375-95-1	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononanoic acid	C(=O)(C(C(C(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F) F)(F)F)(F)F)O
	C10HF19O2	1	335-76-2	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluorodecanoic acid	C(=O)(C(C(C(C(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)O
	C12HF23O2	1	307-55-1	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-tricosafluorododecanoic acid	C(=O)(C(C(C(C(C(C(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)O
Class 2 PFSAs	C6HF13O3S	1	355-46-4	1,1,2,2,3,3,3,4,4,5,5,6,6,6-tridecafluorohexane-1-sulfonic acid	C(C(C(C(F)(F)S(=O)(=O)O)(F)F)(F)F)(C(C(F)(F)F)(F)F)(F)F
	C8HF17O3S	1	1763-23-1	1,1,2,2,3,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonic acid	C(C(C(C(C(F)(F)S(=O)(=O)O)(F)F)(F)F)(F)F)(C(C(C(F)(F)F)(F)F)(F)F)(F)F
Class 3 n:2 FTSs	C8H5F13O3S	1	27619-97-2	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulfonic acid	OS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
Class 4 Cl-PFESAs	C8HClF16O4S	1	756426-58-1	2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-hexoxy)-1,1,2,2-tetrafluoro-ethanesulfonic acid	C(C(C(C(F)(F)Cl)(F)F)(F)F)(C(C(OC(C(F)(F)S(=O)(=O) O)(F)F)(F)F)(F)F)(F)F

Class	Formula	Level	CAS Number	IUPAC Name	SMILE
Class 5 diPAPs	C16H9F26O4P	2	57677-95-9	bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) hydrogen phosphate	C(COP(=O)(O)OCCC(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)C(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F
	C18H9F30O4P	2		3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl hydrogen phosphate	C(COP(=O)(O)OCCC(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)C(C(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F

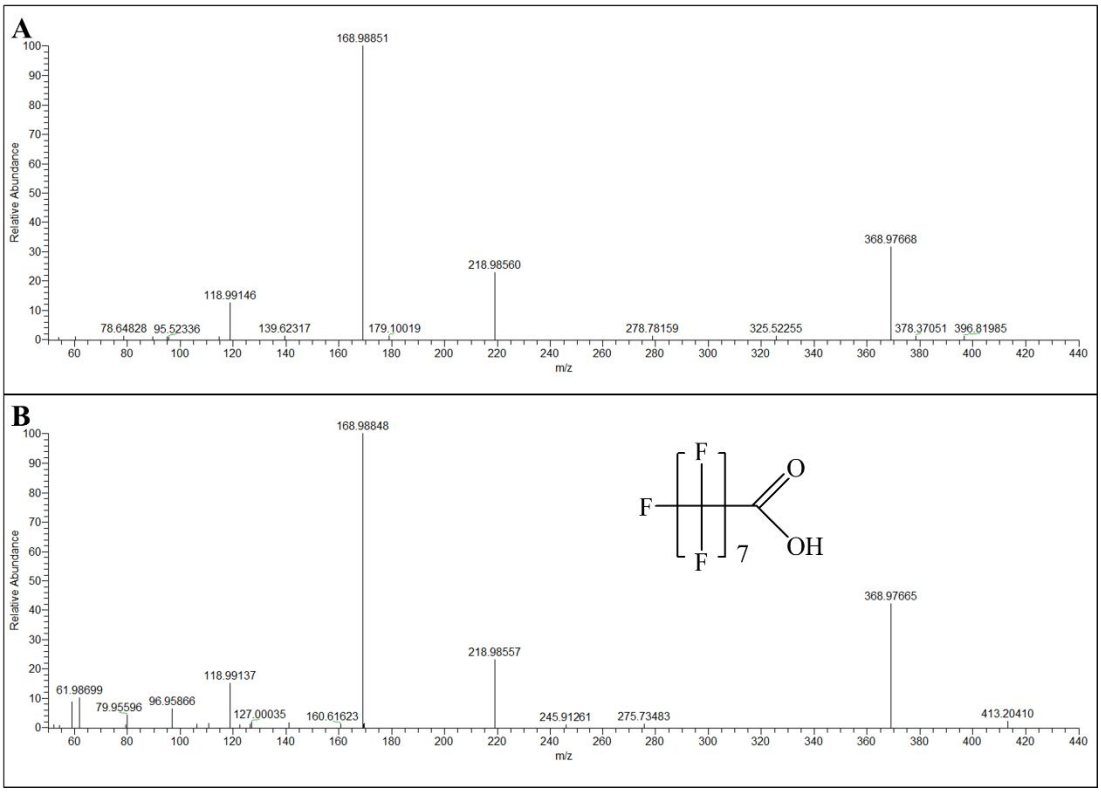


Figure S1. Identification of PFOA (m/z 412.96643). (A) MS/MS spectrum of PFOA in standard. (B) MS/MS spectrum of PFOA in sample.

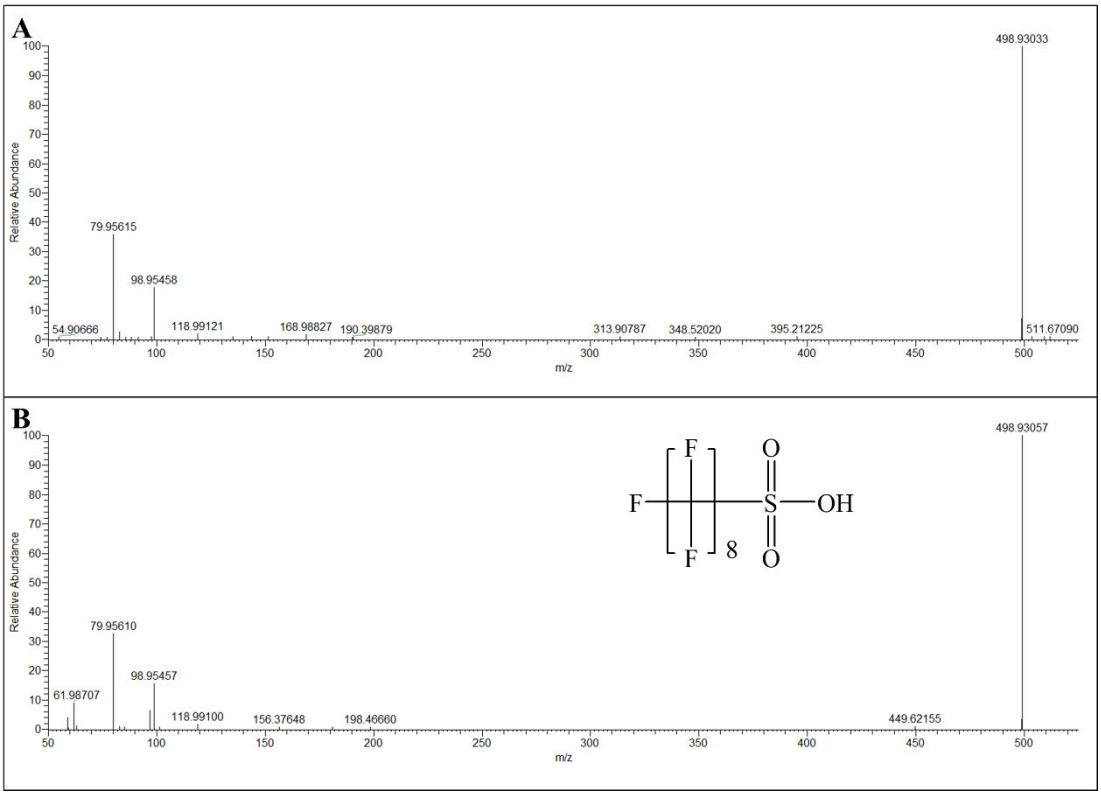


Figure S2. Identification of PFOS (m/z 498.93021). (A) MS/MS spectrum of PFOS in standard. (B) MS/MS spectrum of PFOS in sample.

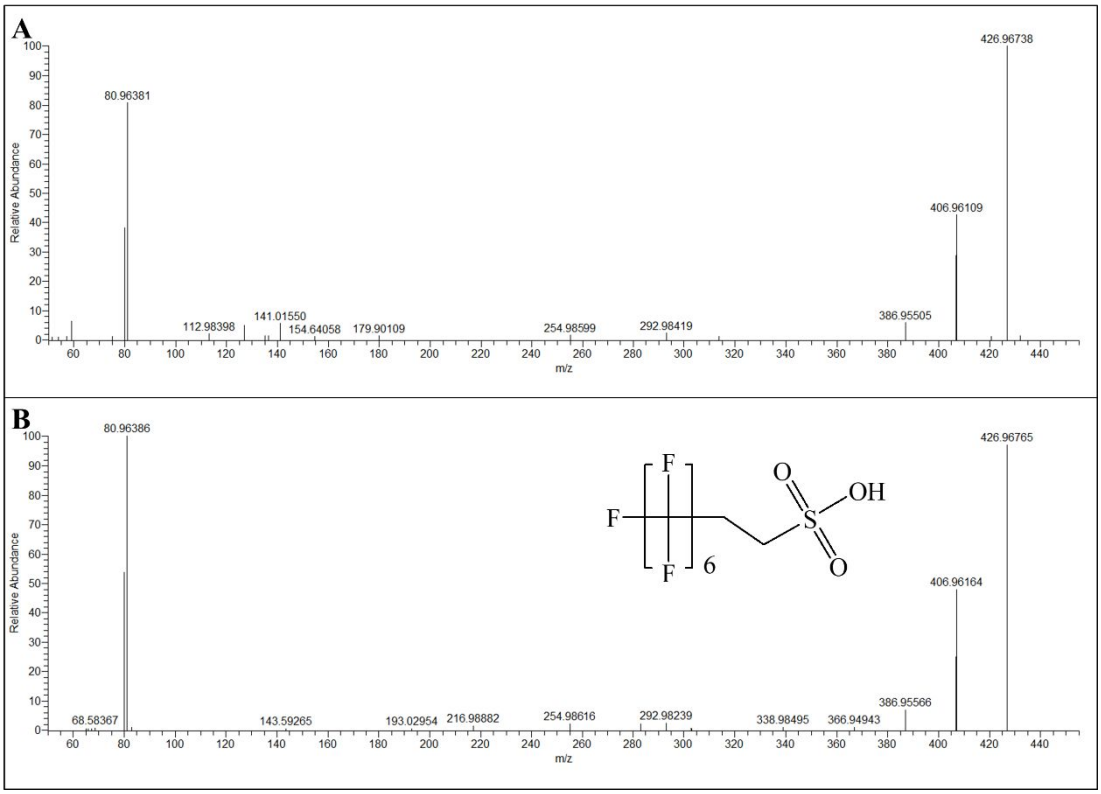


Figure S3. Identification of 6:2 FTS (m/z 426.96791). (A) MS/MS spectrum of 6:2 FTS in standard. (B) MS/MS spectrum of 6:2 FTS in sample.

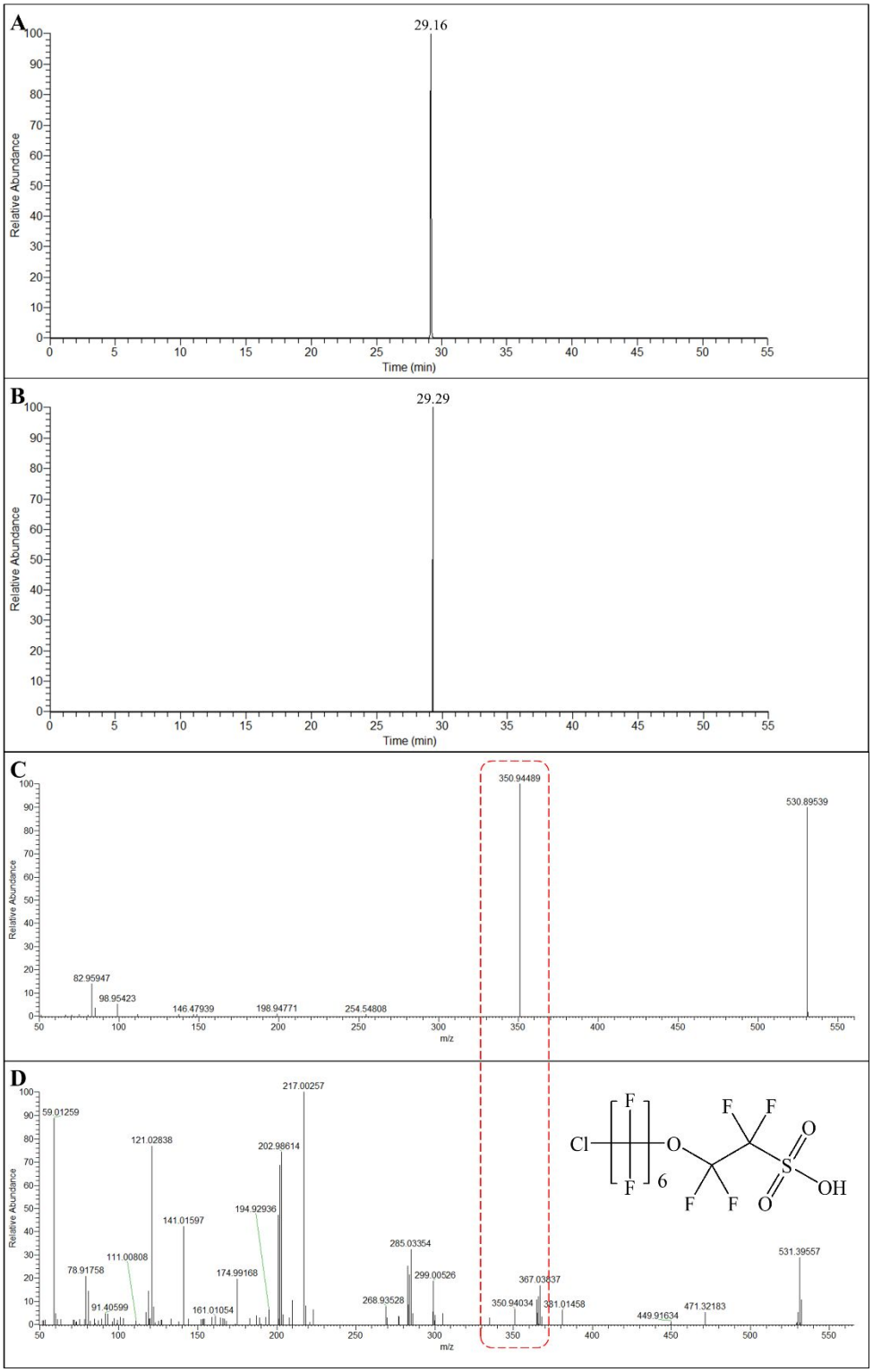
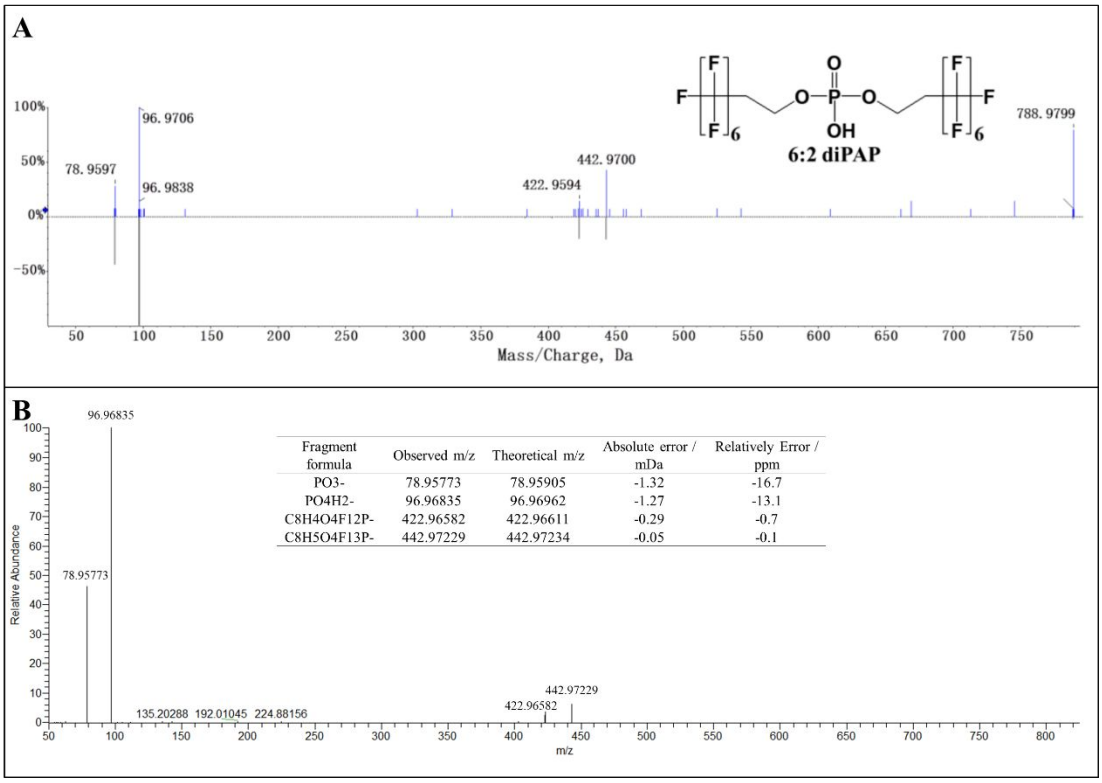


Figure S4. Identification of 6:2 Cl-PFESA (m/z 530.89558). (A) Extract ion chromatogram of 6:2 Cl-PFESA in standard. (B) Extract ion chromatogram of 6:2 Cl-

PFESA in sample. (C) MS/MS spectrum of 6:2 Cl-PFESA in standard. (D) MS/MS spectrum of 6:2 Cl-PFESA in sample.



Fragment formula	Observed m/z	Theoretical m/z	Absolute error / mDa	Relatively Error / ppm
PO3-	78.95773	78.95905	-1.32	-16.7
PO4H2-	96.96835	96.96962	-1.27	-13.1
C8H4O4F12P-	422.96582	422.96611	-0.29	-0.7
C8H5O4F13P-	442.97229	442.97234	-0.05	-0.1

Figure S5. Identification of 6:2 diPAP (m/z 788.97505). (A) MS/MS spectrum of 6:2 diPAP in previous study confirmed by standard.[1] (B) MS/MS spectrum of 6:2 diPAP in sample.

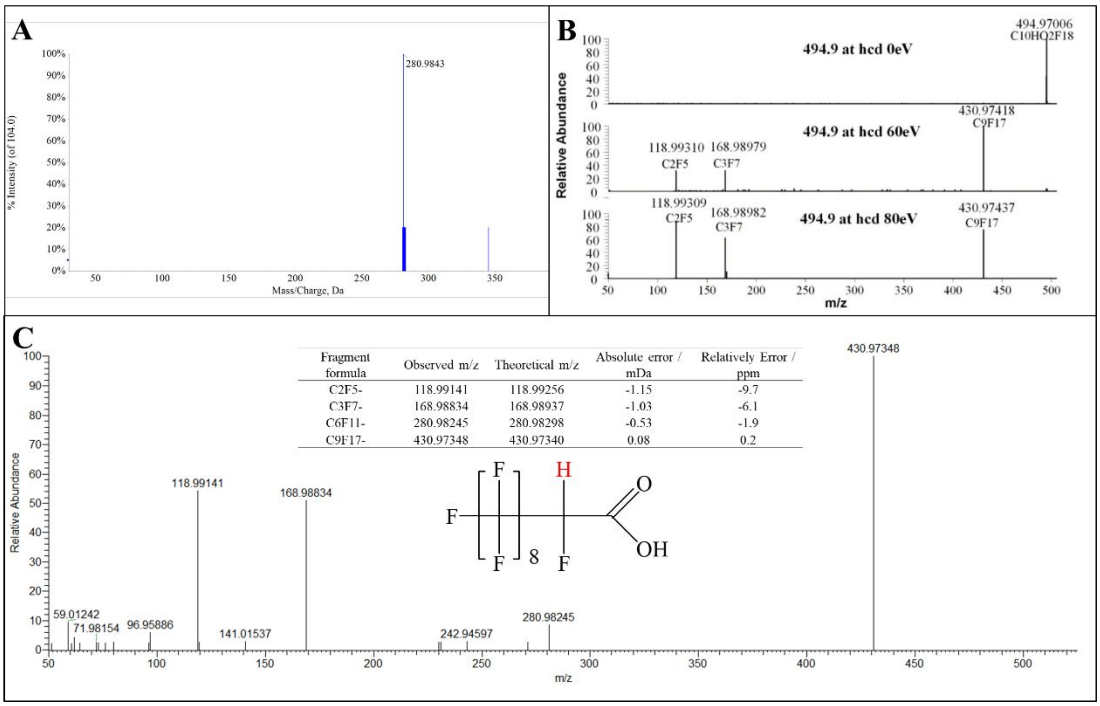
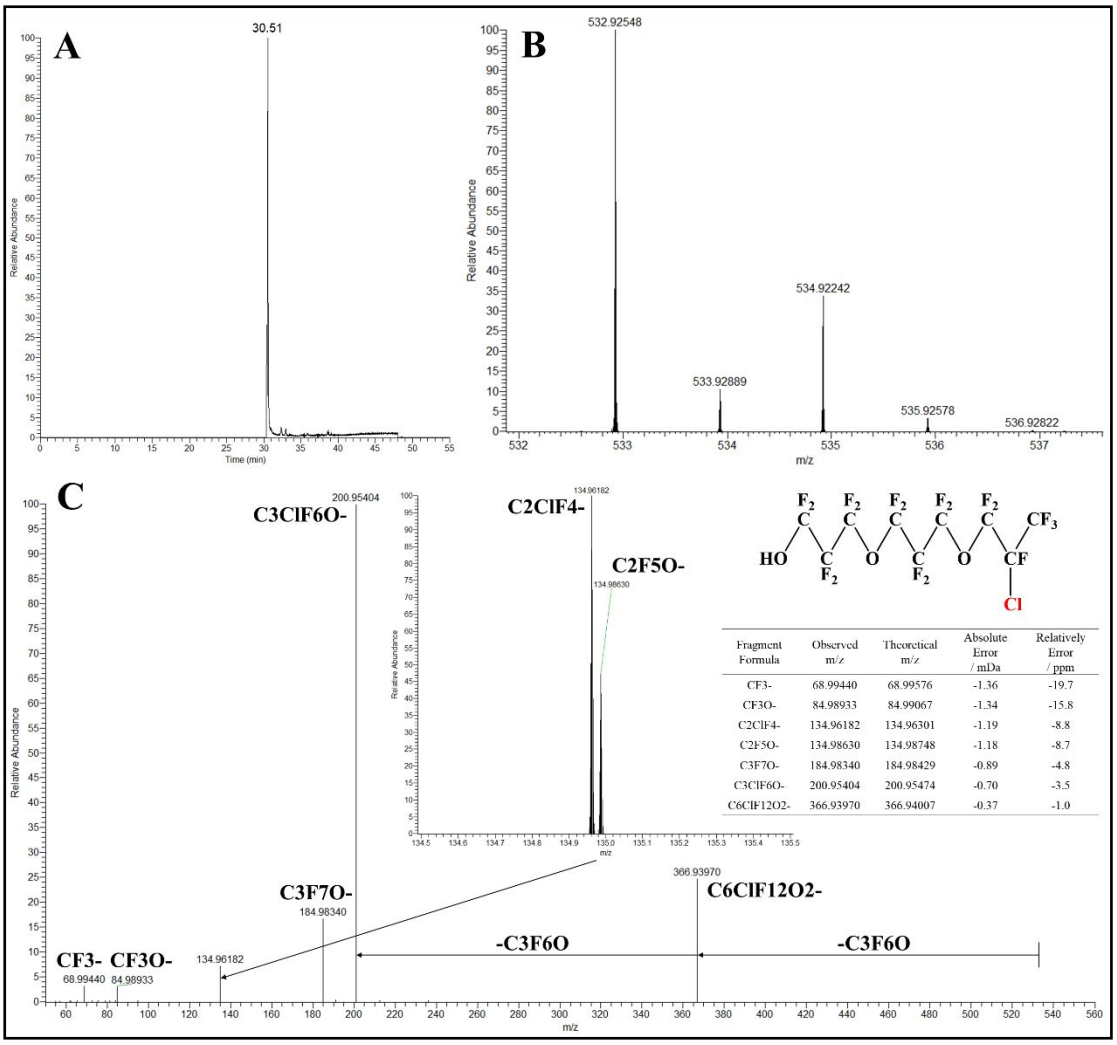


Figure S6. Identification of H-PFCA. (A) MS/MS spectrum of C7 H-PFCA standard (C7H2F12O2, m/z 344.97904). (B) MS/MS spectrum of C10 H-PFCA (C10H2F18O2, m/z 494.96946) under different energies in previous article.[5] (C) MS/MS spectrum of C10 H-PFCA in sample.



Fragment Formula	Observed m/z	Theoretical m/z	Absolute Error / mDa	Relatively Error / ppm
CF3-	68.99440	68.99576	-1.36	-19.7
CF3O-	84.98933	84.99067	-1.34	-15.8
C2ClF4-	134.96182	134.96301	-1.19	-8.8
C2F5O-	134.98630	134.98748	-1.18	-8.7
C3F7O-	184.98340	184.98429	-0.89	-4.8
C3ClF6O-	200.95404	200.95474	-0.70	-3.5
C6ClF12O2-	366.93970	366.94007	-0.37	-1.0

Figure S7. Identification of G03 (m/z 532.92540) in Class 7. (A) Extract ion chromatogram of G03. (B) Isotope distribution of G03 in MS spectrum. (C) MS/MS spectrum of G03 with mass errors for the MS/MS fragments shown in the table.

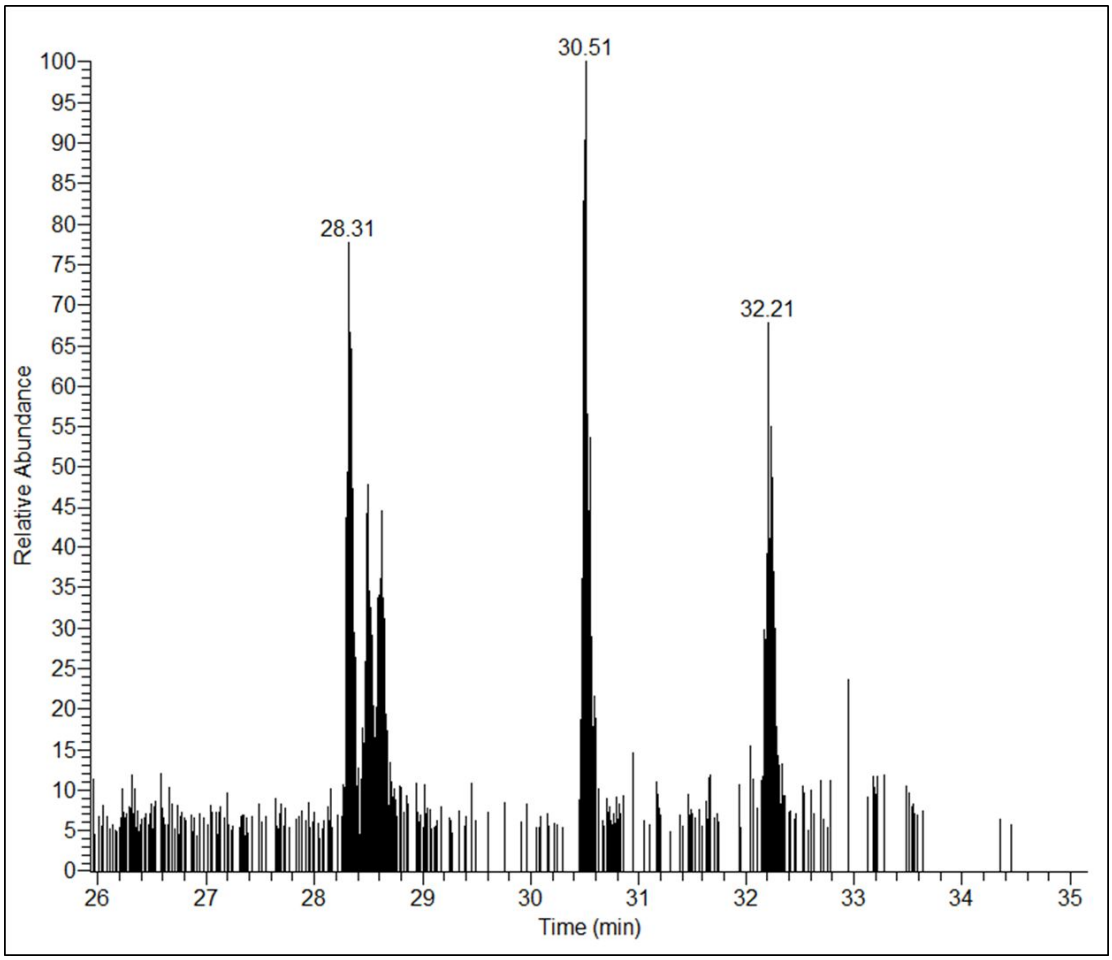
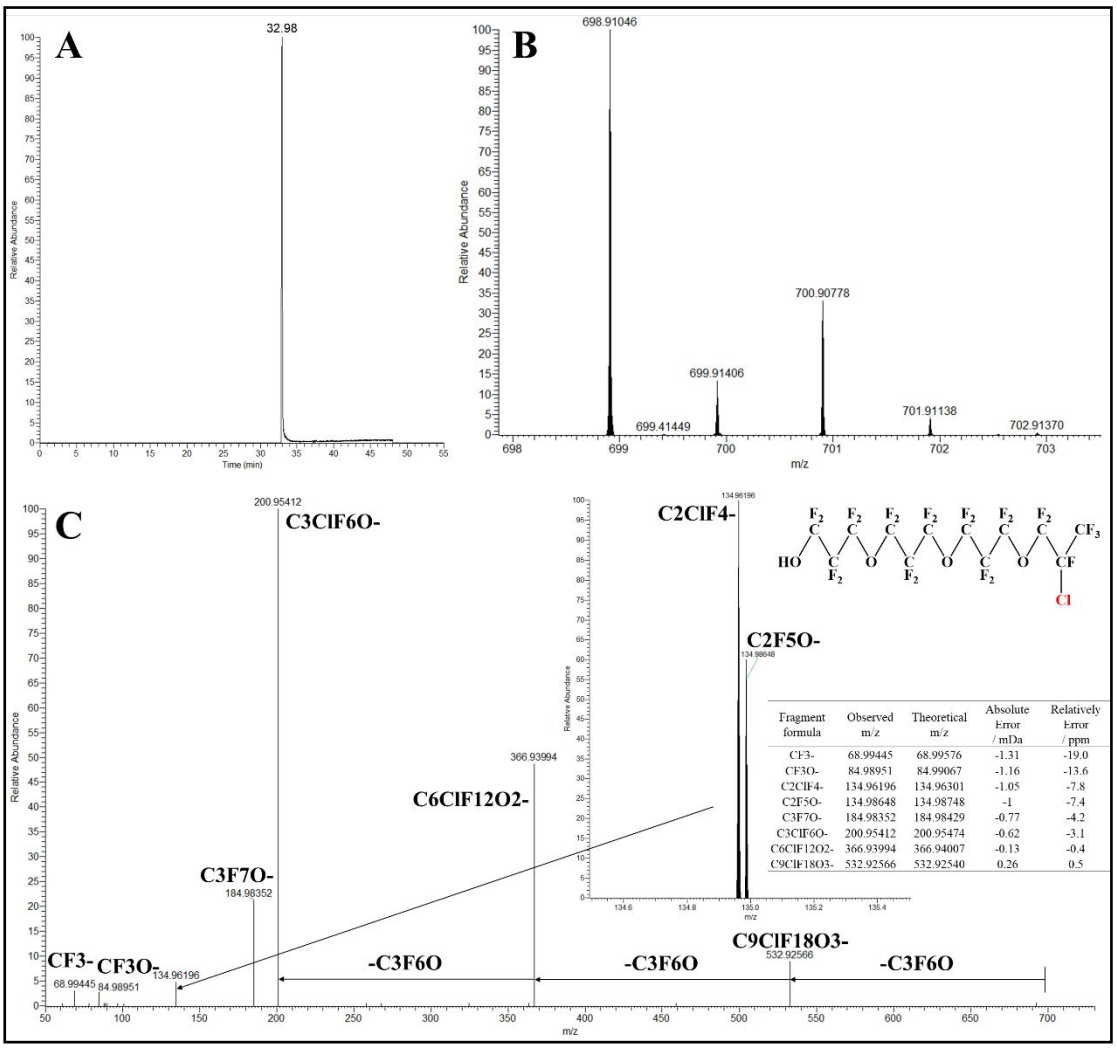
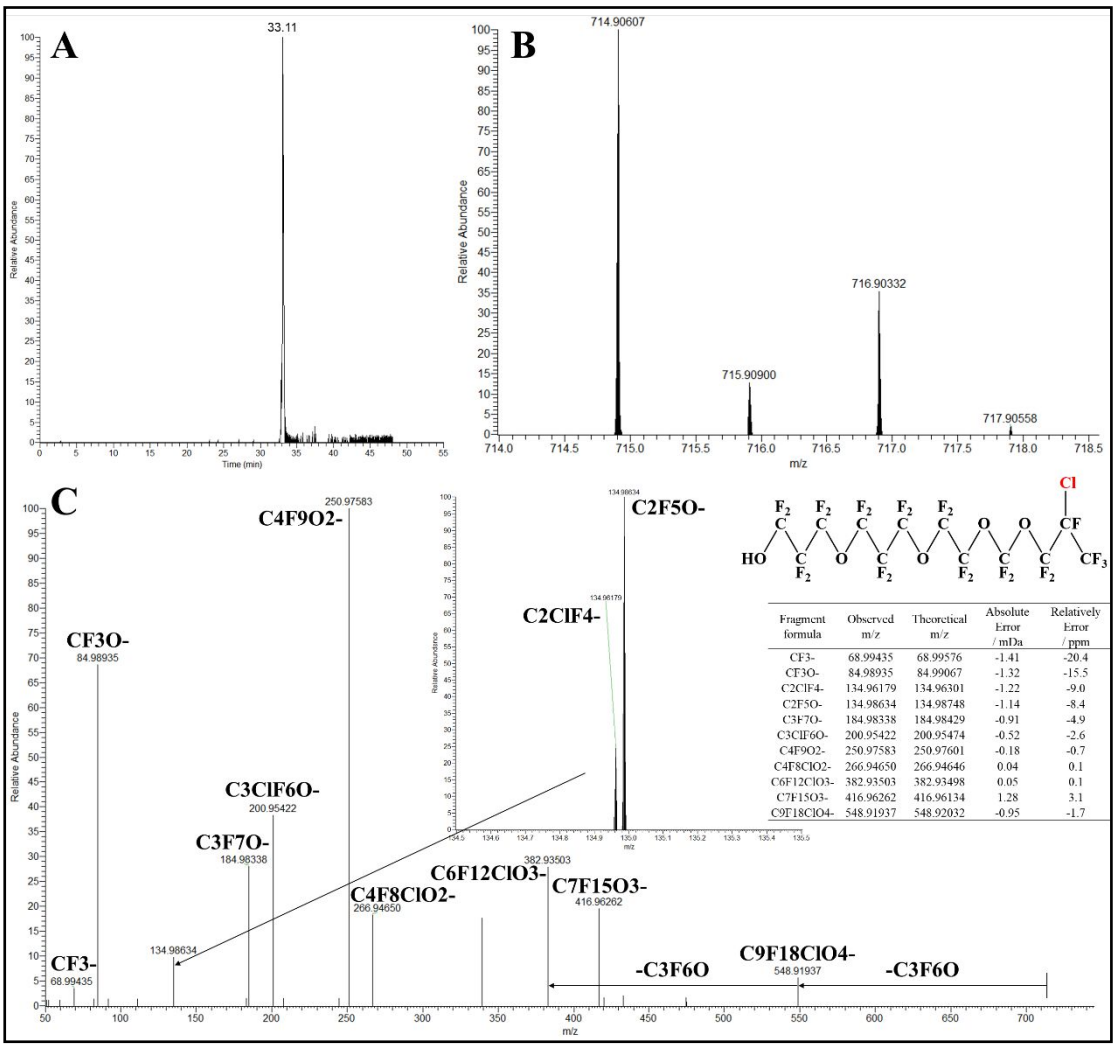


Figure S8. Extract ion chromatogram of G01 (m/z 432.93179) in Class 7.



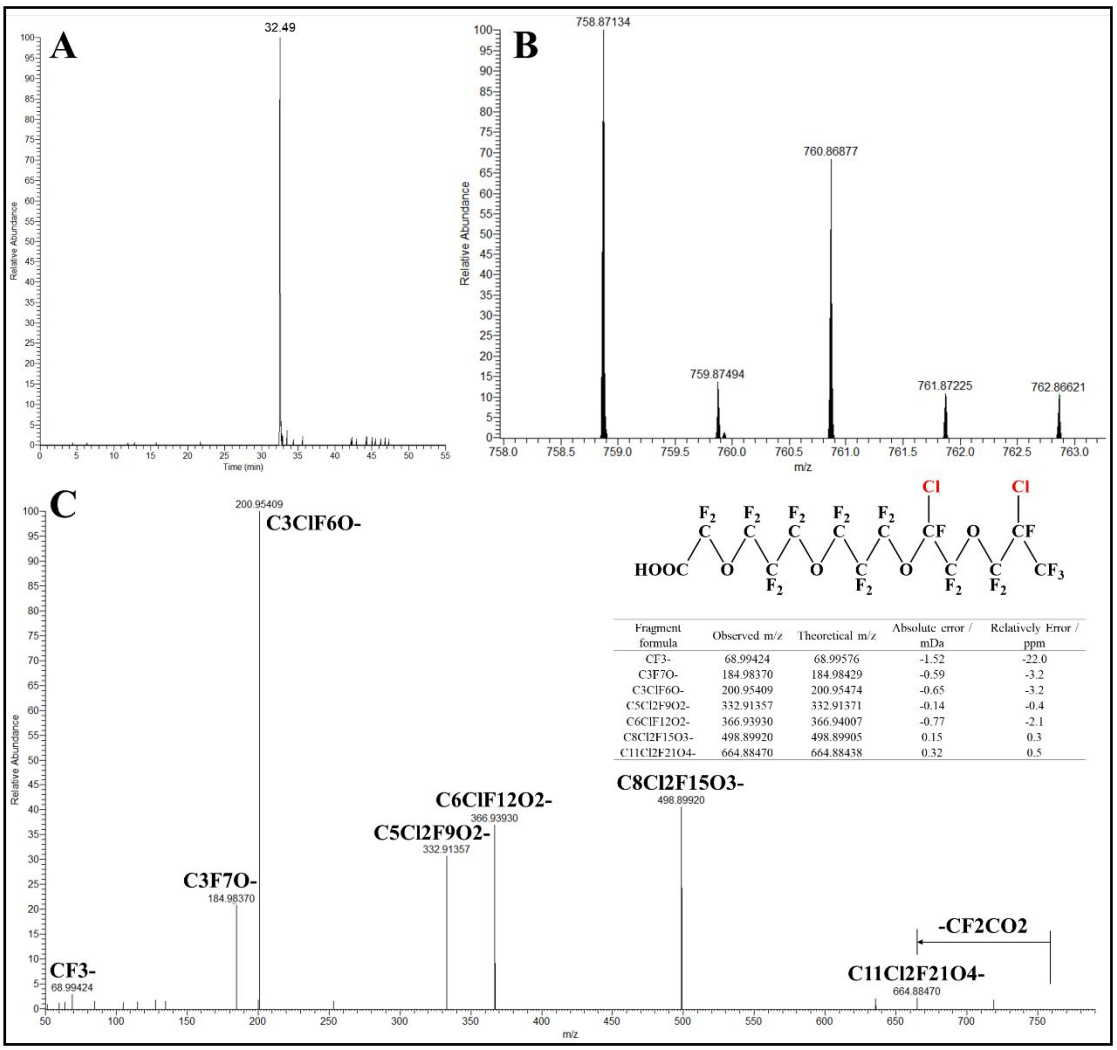
Fragment formula	Observed m/z	Theoretical m/z	Absolute Error / mDa	Relatively Error / ppm
CF3-	68.99445	68.99576	-1.31	-19.0
CF3O-	84.98951	84.99067	-1.16	-13.6
C2ClF4-	134.96196	134.96301	-1.05	-7.8
C2F5O-	134.98648	134.98748	-1	-7.4
C3F7O-	184.98352	184.98429	-0.77	-4.2
C3ClF6O-	200.95412	200.95474	-0.62	-3.1
C6ClF12O2-	366.93994	366.94007	-0.13	-0.4
C9ClF18O3-	532.92566	532.92540	0.26	0.5

Figure S9. Identification of H04 (m/z 698.91074) in Class 8. (A) Extract ion chromatogram of H04. (B) Isotope distribution of H04 in MS spectrum. (C) MS/MS spectrum of H04 with mass errors for the MS/MS fragments shown in the table.



Fragment formula	Observed m/z	Theoretical m/z	Absolute Error / mDa	Relatively Error / ppm
CF3-	68.99435	68.99576	-1.41	-20.4
CF3O-	84.98935	84.99067	-1.32	-15.5
C2ClF4-	134.96179	134.96301	-1.22	-9.0
C2F5O-	134.98634	134.98748	-1.14	-8.4
C3F7O-	184.98338	184.98429	-0.91	-4.9
C3ClF6O-	200.95422	200.95474	-0.52	-2.6
C4F9O2-	250.97583	250.97601	-0.18	-0.7
C4F8ClO2-	266.94650	266.94646	0.04	0.1
C6F12ClO3-	382.93503	382.93498	0.05	0.1
C7F15O3-	416.96262	416.96134	1.28	3.1
C9F18ClO4-	548.91937	548.92032	-0.95	-1.7

Figure S10. Identification of I02 (m/z 714.90565) in Class 9. (A) Extract ion chromatogram of I02. (B) Isotope distribution of H04 in MS spectrum. (C) MS/MS spectrum of I02 with mass errors for the MS/MS fragments shown in the table.



Fragment formula	Observed m/z	Theoretical m/z	Absolute error / mDa	Relatively Error / ppm
CF3-	68.99424	68.99576	-1.52	-22.0
C3F7O-	184.98370	184.98429	-0.59	-3.2
C3ClF6O-	200.95409	200.95474	-0.65	-3.2
C5Cl2F9O2-	332.91357	332.91371	-0.14	-0.4
C6ClF12O2-	366.93930	366.94007	-0.77	-2.1
C8Cl2F15O3-	498.89920	498.89905	0.15	0.3
C11Cl2F21O4-	664.88470	664.88438	0.32	0.5

Figure S11. Identification of J02 (m/z 758.87102) in Class 10. (A) Extract ion chromatogram of J02. (B) Isotope distribution of H04 in MS spectrum. (C) MS/MS spectrum of J02 with mass errors for the MS/MS fragments shown in the table.

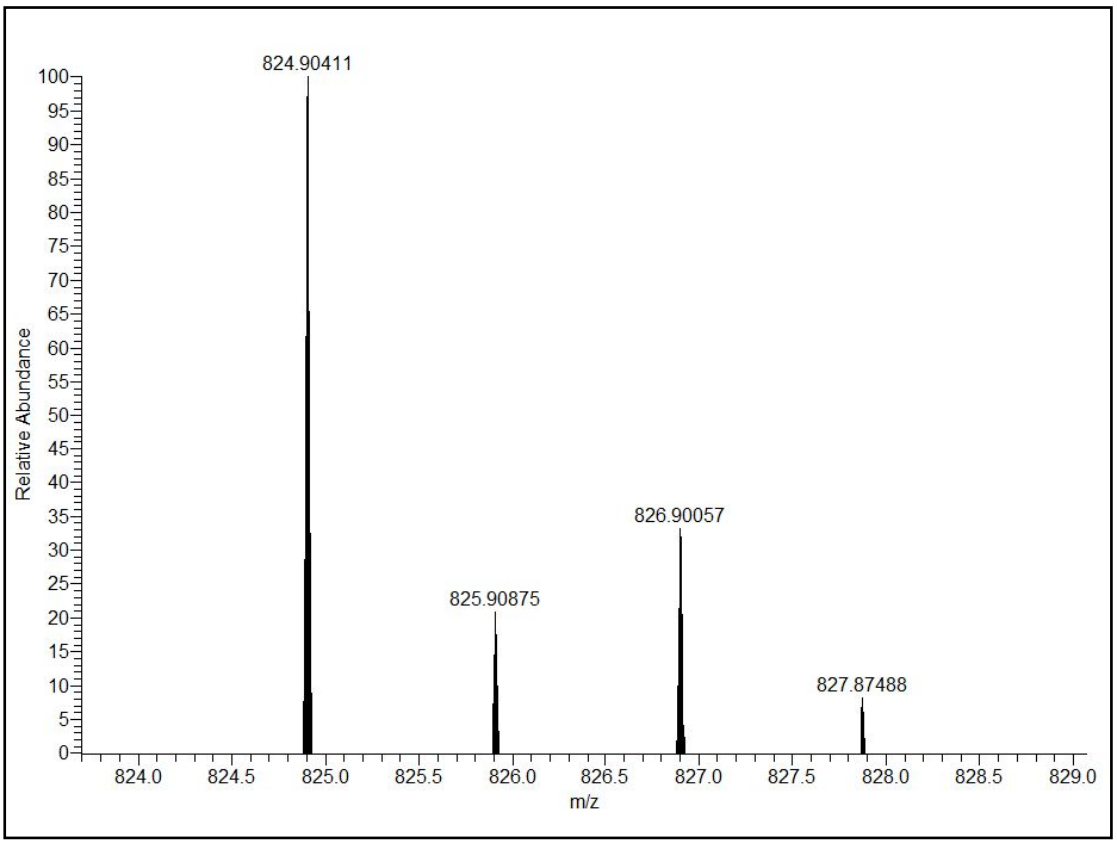


Figure S12. Isotope distribution of K02 (m/z 824.9036) in Class 11.

Table S7. Potential PFASs homologues found as Level 5. The numbers in the "Particulate Matter" and "Gaseous Phase" show the distribution ratio in each phase and were converted by chromatographic peak area.

Homologue	Observe Molecular Weight	RT / min	Particulate Matter				Gaseous Phase
			> 10μm	10-2.5μm	2.5-1μm	< 1μm	
Class 14	208.03662	6.72		0.21	0.49	0.30	0.002
	758.00050	36.89		0.29		0.29	0.42
	807.99647	37.51		0.58	0.42		
Class 15	222.08883	14.57		0.15	0.45	0.36	0.03
	372.07811	15.40					1
Class 16	132.07754	3.63		0.13		0.17	0.70
	232.07074	11.40					1
	332.06392	33.84	0.42		0.19		0.40
Class 17	136.09265	7.29					1
	186.08847	11.32					1
	386.07585	29.35					1
Class 18	198.02702	10.82	0.30	0.20	0.19	0.30	0.002
	298.01903	17.47					1
	398.01332	23.00					1
Class 19	284.08726	12.50		0.02	0.97	0.01	0.002
Class 20	244.13081	10.27					1
	394.12230	25.77					1
	594.10933	28.95	1				
Class 21	238.12007	16.55					1
	288.11317	19.14					1
	388.10713	19.36					1
	488.10011	25.77					1
	588.09968	28.22					1
Class 22	176.10397	6.46		0.05	0.23	0.15	0.57
	326.09361	12.04					1
	376.09160	26.74					1
Class 23	128.08260	11.34					1
	278.07249	17.04					1
	378.06840	26.01					1
Class 24	160.10901	7.41	0.007	0.04	0.11	0.14	0.70
	310.09868	11.77					1
	410.09385	24.05					1
Class 25	166.09851	17.15					1
	316.08824	18.56					1
	466.08064	18.61					1

Homologue	Observe Molecular Weight	RT / min	Particulate Matter				Gaseous Phase
			> 10μm	10-2.5μm	2.5-1μm	< 1μm	
Class 26	339.12562	14.83					1
	389.12352	18.96					1
Class 27	180.07770	16.53		0.48	0.52		
	330.06755	22.57					1
	480.05958	23.54					1
Class 28	181.10945	16.35					1
	331.09913	17.77					1
	381.09672	24.98					1
Class 29	343.09901	10.89					1
	443.09422	26.90					1
Class 30	214.11352	19.90					1
	264.11101	20.74					1
	314.10899	25.93					1
Class 31	224.06804	10.25					1
	324.06108	10.62					1
	374.06093	13.52					1
Class 32	242.10892	12.40					1
	342.10390	24.88					1
Class 33	244.02571	2.04		0.73			0.27
Class 34	247.08423	13.93					1
	347.07634	20.57					1
	397.07408	34.07					1
Class 35	250.12022	16.72	0.12	0.03	0.23	0.01	0.62
	400.10936	19.89					1
	450.10740	31.16					1
Class 36	268.13112	15.57					1
	418.12022	20.06					1
	618.11030	23.80					1
Class 37	295.05156	17.20					1
	345.04939	21.74					1
	395.04323	22.59					1
Class 38	378.12501	23.92					1
	478.11717	24.98					1
	578.11244	31.82					1

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