Supporting Information

Non-Target and Suspect Screening of Per- and Polyfluoroalkyl Substances in Airborne Particulate Matter in China

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Section 1. Standards and reagents.

The detail information on PFASs standards is listed in **Table S1**. Ammonium acetate (HPLC grade) was purchased from CNW technologies GmbH (Duesseldorf, Germany). N-methylpiperdine (HPLC grade, purity: 99%) was purchased from Sigma (USA). Formic acid (HPLC grade, purity: 99%) was purchased from ROE SCIENTIFIC ING (USA). Methanol (HPLC grade, purity: 99.9%) was purchased from Merck (Germany). The additional PFCA or PFSA homologues were checked for all standards, and the errors of quantitation were controlled in 0.6% (**Table S2**). ISO 21675 standard from Wellington Laboratories was used for the identification of PFASs in QTOF data. This standard was prepared for the Interlaboratory trial for validation of ISO 21675 for PFAS in water, which contained 30 native PFAS standards including 13 PFCAs, 5 PFSAs, 2 n:2FTSs, 2 PFECAs, FOSA, N-MeFOSA, N-EtFOSA, N-MeFOSAA, N-EtFOSAA, FOEUA, 6:2 Cl-PFESA, 8:2 diPAP.

Table S1: The abbreviations, supplier and purity of PFASs standards and internal standards

	Compound name	Abbreviation	Supplier	Purity
Analyte	Perfluoropentanoate	PFPeA	Sigma-Aldrich	97%
	Perfluorohexanoate	PFHxA	Sigma-Aldrich	97%
	Perfluoroheptanoate	PFHpA	Sigma-Aldrich	99%
	Perfluorooctanoate	PFOA	Alfa Aesar	95%
	Perfluorononanoate	PFNA	Alfa Aesar	97%
	Perfluorodecanoate	PFDA	Sigma-Aldrich	98%
	Perfluoroundecanoate	PFUnDA	Sigma-Aldrich	95%
	Perfluorododecanoate	PFDoDA	Sigma-Aldrich	95%
	Perfluorotridecanoate	PFTrDA	Sigma-Aldrich	97%
	Perfluorotetradecanoate	PFTeDA	Sigma-Aldrich	97%
	Perfluorobutane sulfonate	PFBS	Woke	98%
	Perfluorohexane sulfonate	PFHxS	Sigma-Aldrich	98%
	n-perfluoro-1-octanesulfonate	PFOS	Wellington Laboratories	98%
	Sodium bis(1H,1H,2H,2H-perfluorooctyl)phosphate	6:2diPAP	Wellington Laboratories	98%
Internal Standards	Perfluoro-n-[1,2-13C2]hexanoic acid	MPFHxA	Wellington Laboratories	98%
	Perfluoro-n-[1,2,3,4-13C4]octanoic acid	MPFOA	Wellington Laboratories	99%
	Perfluoro-n-[1,2,3,4,5-13C5]nonanoic acid	MPFNA	Wellington Laboratories	98%
	Perfluoro-n-[1,2-13C2]decanoic acid	MPFDA	Wellington Laboratories	98%
	Perfluoro-n-[1,2-13C2]undecanoic acid	MPFUnDA	Wellington Laboratories	98%
	Perfluoro-n-[1,2,3,4-13C4]dodecanoic acid	MPFDoDA	Wellington Laboratories	98%
	Sodium perfluoro-1-hexane[18O2]sulfonate	MPFHxS	Wellington Laboratories	98%
	Sodium perfluoro-1-[1,2,3,4-13C4]octanesulfonate	MPFOS	Wellington Laboratories	99%
	Sodium bis(1H,1H,2H,2H-[1,2-13C2]perfluorodecyl)phosphate	M8:2diPAP	Wellington Laboratories	99%

Table S2. The percentage of additional PFCA or PFSA homologues in each PFASs standard and the error of the mixture standard for quantitative analysis.

PFASs standard	PFBS	PFHxS	PFOS	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
PFBS	/	-	-	-	-	-	-	-	-	-	-	-	-
PFHxS	0.42%	/	-	-	-	-	-	-	-	-	-	-	-
PFOS	-	-	/	-	-	-	-	-	-	-	-	-	-
PFPeA	-	-	-	/	-	0.26%	-	-	-	-	-	-	-
PFHxA	0.20%	0.22%	-	-	/		-	-	-	-	-	-	-
PFHpA	-	-	-	-	-	/	-	-	-	-	-	-	-
PFOA	-	-	-	-	0.52%	-	/	-	-	-	-	-	-
PFNA	-	-	-	-	-	0.25%	-	/	-	-	-	-	-
PFDA	-	-	-	-	-	-	-	-	/	-	-	-	-
PFUnDA	-	-	-	-	-	-	-	-	-	/	-	-	-
PFDoDA	-	-	-	-	-	-	0.21%	0.22%	-	-	/	-	-
PFTrDA	-	-	-	-	-	-	-	-	-	-	-	/	0.29%
PFTeDA	-	-	-	-	-	-	-	-	-	-	-	-	/
Mix standard	0.62%	0.22%	0.00%	0.00%	0.52%	0.51%	0.21%	0.22%	0.00%	0.00%	0.00%	0.00%	0.29%

Section 2. Sample Preparation.

Sample preparation was modified based on previous study[1]. Each particle-size fraction of both samplers was extracted separately. For extraction, samples were placed into 15mL polypropylene centrifuge tubes and spiked with mass-labelled PFASs including MPFHxA, MPFOA, MPFNA, MPFDA, MPFUnA, MPFDoA, MPFHxS, MPFOS and M8:2diPAP. Each internal standard was 0.5 ng except for M8:2diPAP which was 1 ng. Extraction was performed four cycles by 40℃ ultrasonic bath, and during each cycle it took 10 min and 5 mL, 5 mL, 5 mL and 3 mL of methanol, respectively. After each extraction step, samples were centrifuged for 5 min at 5000 rpm. Supernatants of each sample were combined in a separate polypropylene centrifuge tube and was reduced to a volume of 1 mL by evaporation under a gentle stream of nitrogen. Then the concentrated extracts were further cleaned up with a Supelclean ENVI-carb cartridge (Supelco, Bellfonte, USA). The cartridge was pre-cleaned with 3 mL of methanol, the extract was added and eluted with 3 mL of methanol. The 4 mL of extract and eluate were collected and then concentrated again to 0.5 mL 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).

For non-target analysis, 100 μL filtrate of each fraction was combined and re-concentrated into 100 μL. While, for target analysis each fraction was analysed separately. A volume of 100 μL of filtrate and 100 μL of 2mM ammonium acetate was transferred into a polypropylene vial for PFCAs and PFSAs analysis. A volume of 170 μL of filtrate and 30 μL of diluent-A (a mixture of formic acid, N-methylpiperdine and

Milli-Q water, the value of $V_{formic\ acid}$: $V_{N\text{-}methylpiperidine}$: $V_{Milli\text{-}Q\ water}$ was 7:20:200) was transferred into a polypropylene vial for diPAPs analysis.

Section 3. Instruments Analysis for target PFASs analysis.

Instrumental analysis for PFCAs and PFSAs. PFCAs and PFSAs were determined by high performance liquid chromatography (HPLC; Agilent Technologies, Waldbronn, Germany) – tandem mass spectrometry with an electrospray ionization (ESI) source (API-4000, ABSciex, Darmstadt, Germany). A PFAS isolator was set to reduce the instrument background. A BEH C18 column (2.1 mm×50 mm, 2.5 μm, Waters, U.S.) held at 40 °C was used to separate target analyte. The mobile phases used were 2mM ammonium acetate in water (A) and methanol (B). The gradient was set as follows: 10 μL aliquot of sample was injected into HPLC-MS/MS and the flow rate was set 400 μL/min with starting at 95% of solvent A held until 0.50 min, then decreased to 80% of solvent A until 1.5 min, then decreased to 50% of solvent A until 5 min, then decreased to 35% of solvent A until 13 min, then decreased to 15% of solvent A until 14.5 min, then decreased to 0% of solvent A until 15.5 min, then increased to 95% of solvent A until 15.6 min, then kept 95% of solvent A until 18 min for equilibration.

The mass spectrometer was operated in the negative ion mode with multiple reaction monitoring (MRM). The source temperature was set at 400 ℃, and the IonSpray Voltage was set to -4500 V. The curtain gas, nebulizer gas and drying gas pressures were 15, 55 and 55 psi, respectively. For each compound except for PFPeA, two MRM-transitions were monitored. Other parameters such as precursor/product ions, declustering potential (DP) and collsion energy (CE) were shown in **Table S3.**

Instrumental analysis for diPAPs. Instruments used in diPAPs analysis were same as PFCAs and PFSAs. The mobile phases used were 5mM N-methylpiperdine in water (A)

and methanol (B). The gradient was set as follows: 5 μL aliquot of sample was injected into HPLC-MS/MS and the flow rate was set 400 μL/min with starting at 95% of solvent A held until 0.50 min, then decreased to 70% of solvent A until 1 min, then decreased to 15% of solvent A until 6 min, then decreased to 0% of solvent A until 8.5 min, then kept 0% of solvent A until 9.5 min, then increased to 95% of solvent A until 9.6 min, then kept 95% of solvent A until 19min for equilibration.

The mass spectrometry was operated in the negative ion mode with MRM. The source temperature was set at 600 ℃, and the ionspray voltage was set to -4500 V. The curtain gas, nebulizer gas and drying gas pressures were 15, 55 and 55 psig, respectively. Other details were seen in **Table S3.**

Table S3: MS parameter, procedural blank, LOQ, and procedural recovery for target analysis

analyte	declustering potential (V)	Collision Energy (V)	Precursor ion	Product ion	Internal Standard	Procedural blank (n=6)	LOQ[a]	Procedural recovery(n=4)	
								Mean	SD
PFBS	-78 -82	-57 -43	298.8	79.9 98.9	**MPFHxS**	ND [a]	0.05	95.0%	0.10
PFHxS	-98 -98	-79 -56	399.0	80.1 98.9	**MPFHxS**	ND	0.05	90.2%	0.08
PFOS	-105 -105	-95 -75	498.7	80.0 98.9	**MPFOS**	ND	0.05	96.6%	0.21
PFPeA	-36	-12	262.8	218.5	**MPFHxA**	ND	0.05	90.0%	0.12
PFHxA	-45 -42	-13 -30	323.2	268.7 119.0	**MPFHxA**	ND-<1/2LOQ	0.13	103%	0.06
PFHpA	-35 -40	-14 -26	362.9	318.8 168.9	**MPFOA**	ND-<1/2LOQ	0.05	85.2%	0.08
PFOA	-43 -43	-15 -27	413.1	368.8 168.9	**MPFOA**	ND-<1/2LOQ	0.05	88.9%	0.12
PFNA	-39 -47	-16 -25	436.0	418.8 18.8	**MPFNA**	ND-<1/2LOQ	0.09	83.3%	0.12
PFDA	-25 -60	-17 -25	512.8	468.8 218.8	**MPFDA**	ND-<1/2LOQ	0.05	81.0%	0.11
PFUnA	-50 -49	-17 -26	563.0	518.9 269.2	**MPFUnA**	ND-<1/2LOQ	0.05	84.0%	0.12
PFDoDA	-48 -54	-17 -29	613.0	568.8 268.8	**MPFDoDA**	ND	0.05	95.1%	0.20

analyte	declustering potential (V)	Collision Energy (V)	Precursor ion	Product ion	Internal Standard	Procedural blank (n=6)	LOQ[a]	Procedural recovery(n=4)	
								Mean	SD
PFTrA	-57 -58	-19 -31	662.9	618.9 318.8	**MPFDoDA**	ND	0.05	74.9%	0.09
PFTeA	-59 -65	-21 -42	712.9	668.9 168.9	**MPFDoDA**	ND	0.05	80.1%	0.08
6:2diPAP[b]	-85 -85	-28 -70	788.9	442.9 97.0	**M8:2diPAP**	ND	0.1	90.6%	0.11

a: dimensions for procedural blank and LOQ were both μg/L and they represent the levels of procedural blank and LOQ detected in the instrument.
b: the number of procedure blank and procedure recovery were both three.

Section 4. Instruments Analysis for PFASs screening.

PFASs screening was performed on high performance liquid chromatography (HPLC; Agilent Technologies, Waldbronn, Germany) coupled with a high resolution hybrid quadrupole time-of-flight mass spectrometer (Triple TOF 5600, AB Sciex, Foster City, CA) with an electrospray ionization (ESI) source operating in a negative ion mode. A BEH C18 column (2.1 mm×50 mm, 2.5 μm, Waters, U.S.) held at 40 °C was used to separate chemicals. The mobile phases used were 2mM ammonium acetate in 5% methanol aqueous solution (A) and methanol (B). The gradient was set as follows: 5 μL aliquot of sample was injected into LC-Q-TOF-MS and the flow rate was set 400 μL/min with starting at 100% of solvent A and was kept for 1 min, then decreased to 75% of solvent A until 9 min, then decreased to 50% of solvent A until 18 min, then decreased to 25% until 28 min, then decreased to 0% until 39min and kept for 9 min, then increased to 100% of solvent A until 48.1 min, then kept 100% of solvent A until 55 min for equilibration. The information dependent acquisition (IDA) experiment was conducted with a TOF MS full scan analysis (100ms) and up to 20 dependent MS/MS analysis (50ms for each MS/MS analysis) per cycle. The TOF MS full scan was operated with the mass range of *m/z* 50 to 1250, and the dependent MS/MS was operated with the mass range of *m/z* 30 to 1250 under the high-resolution mode. The mass resolution of information-dependent acquisition (including MS and MS/MS scan) is 25,000 FWHM (full width at half maxima) for m/z 100 and 40,000 FWHM for m/z 950. Dynamic Background Subtraction, which enables detection of species as their signal increases in intensity, therefore focusing on detection and analysis of the

precursor ions on the rising portion of the LC peak, up to the top of the LC peaks (maximum intensity), was applied in the IDA criteria for dynamic exclusion. The fragment ions were generated from collision induced dissociation with nitrogen under a standardized collision energy (CE) = -50 V with collision energy spread (CES) = ±10 V. The other experimental parameters were: nebulizer gas (gas 1), 45 psi; heater gas (gas 2), 45 psi; curtain gas, 25 psi; temperature, 550 °C; ionspray voltage floating, -4500 V; declustering potential, -100 V; collision energy, -10 V. All gases used were nitrogen.

Section 5. PFASs Screening and Identification.

All indoor (or outdoor) data were opened with PeakView 1.2 and a procedure blank was set as control. “Enhance peak find” was used to build non-target analysis list with background subtraction. An initial picking based on a: S/N>3; b: intensity>100; was conducted. The peaks with CF2 normalized mass defects for PFASs (> 0.85 or < 0.15) were further identified the homologous series of PFASs. The PFASs homologues were identified by the mass difference of 49.99681 Da (-[CF_2]-) and 99.99362 Da (-[CF_2CF_2]-) among the exact mass of peaks. The mass difference of PFASs homologues was conducted by a matlab script written by authors. In this script, the peak list including exact mass and retention time was the input data, and the homologue candidate list was the output result. During the running of script, the mass difference of any two peaks was calculated. If the mass difference was equal to (CF2)n or (CF2CF2)n (mass error < 5ppm), the two peaks was retained in the homologue candidate list (Figure S1). The extract ion chromatograms (EICs) and retention times (RT) of each series were checked respectively. In each series, an ascending trend of *m/z* vs. retention time (RT) should be observed. To exclude dimers, adducts, and isotopes in the identified PFASs homologues, the exact mass of peaks (mass error < 5ppm) with the same retention time (< 0.1min) were checked. [M+Na-2H]-, [M+K-2H]-, [M+NH4-2H]-, [M+Ac]-, [M+NaAc-H]-, [2M-H]-, [2M+Na-2H], [2M+K-2H], and [2M+NH4-2H] were considered as potential dimers or adducts. Homologues series (over 3 congers) meeting all those rules were further carried out for molecular formulae calculation and structure speculation.

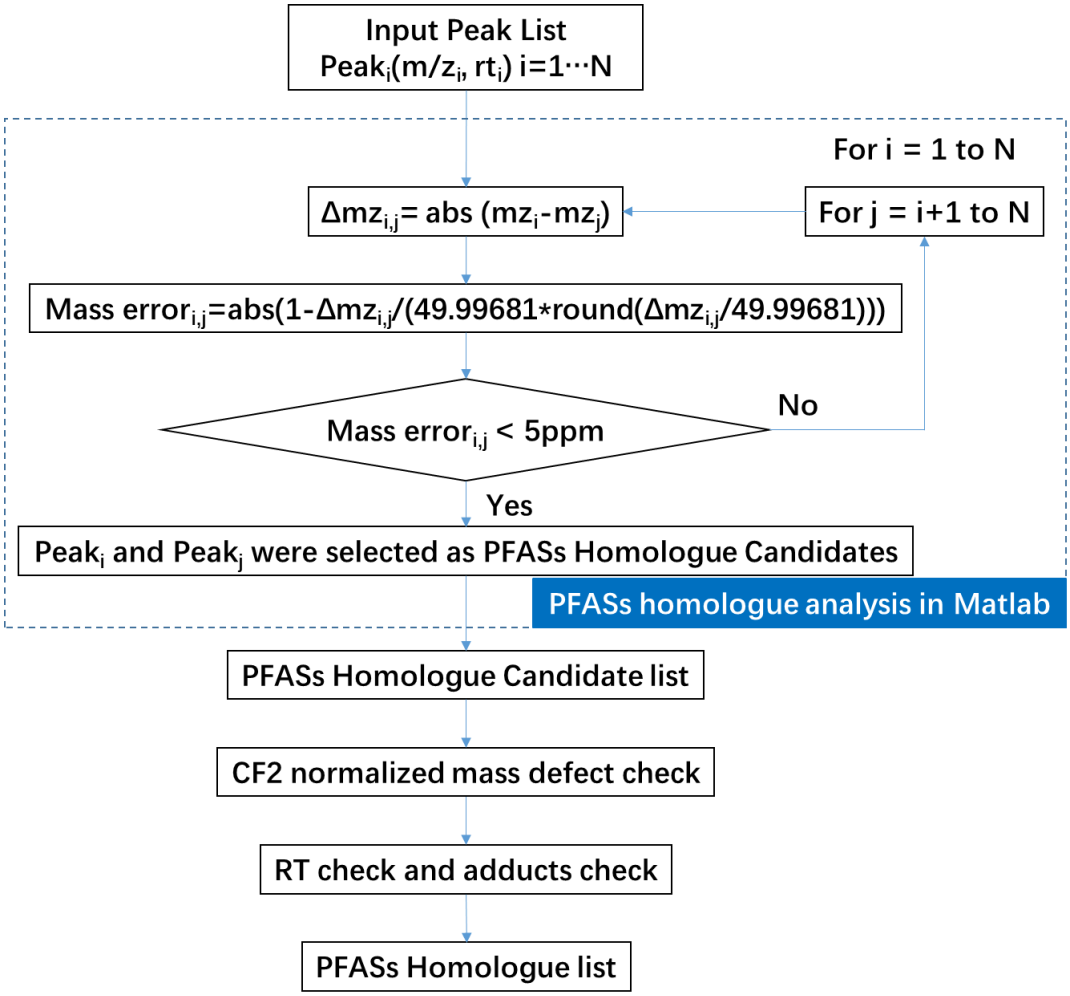
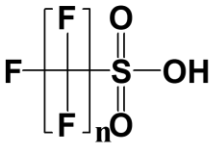


Figure S1. Flowchart of the PFASs homologue analysis.

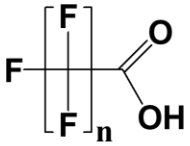
Molecular formulae were calculated using a calculator in PeakView® 1.2 based on accurate mass, isotope distributions, and fragments in MS/MS spectrum (exact mass error < 5 ppm, isotope ratio difference <20%, and fragments mass error < 5 mDa). Parameter settings were based on published methods with some modification.[2,3] The elements setting included C (3-50), H (0-50), F (0-50), O (0-8), P (0-4), S (0-4), Cl (0-2). The number of ring and double bond ranged from 0 to 5. Even-electron state and charge state of -1 ([M-H]-) were selected for the calculation of molecular formulae.

Homologue	Proposed Structure	Formula	level	Observe m/z	error ppm	RT min	RT delta min	Homologue	Proposed Structure	Formula	level	Observe m/z	error ppm	RT min	RT delta min
PFSAs	SA(4)	C4F9SO3H	1	298.9421	-2.9	13.0	0.032	H-PFdiOAs	D(11)	C14H3F23O4	3	670.9586	-0.8	20.8	
	SA(6)	C6F13SO3H	1	398.9356	-2.6	20.6	-0.034		D(12)	C15H3F25O4	4	720.9546	-1.8	22.5	
	SA(7)	C7F15SO3H	4	448.9331	-0.9	22.9		n:2 Cl-PFESAs	E(6)	C8HClF16O4S	1	530.8932	-4.4	25.8	0.037
	SA(8)	C8F17SO3H	1	498.9289	-2.7	24.9	-0.046		E(8)	C10HClF20O4S	2	630.8866	-4.1	28.8	
PFCAs	SB(5)	C6F11O2H	1	312.9718	-3.2	15.7	-0.030	PFdiOAs	F(7)	C9F14O4H2	2	438.9667	2.3	8.1	
	SB(6)	C7F13O2H	1	362.9681	-4.1	19.8	-0.007		F(8)	C10F16O4H2	1	488.9610	-3.1	12.5	0.044
	SB(7)	C8F15O2H	1	412.9647	-4.1	22.4	-0.054		F(9)	C11F18O4H2	2	538.9588	-0.9	15.6	
	SB(8)	C9F17O2H	1	462.9615	-3.8	24.6	-0.052		F(10)	C12F20O4H2	1	588.9554	-1.2	18.1	0.024
	SB(9)	C10F19O2H	1	512.9597	-0.7	26.4	-0.018		F(11)	C13F22O4H2	2	638.9523	-0.9	20.2	
	SB(10)	C11F21O2H	1	562.9548	-3.6	27.8	-0.102		F(12)	C14F24O4H2	2	688.9494	-0.4	21.9	
	SB(11)	C12F23O2H	1	612.9525	-1.8	29.2	0.017		F(13)	C15F26O4H2	2	738.9455	-1.3	23.5	
	SB(12)	C13F25O2H	1	662.9477	-4.2	30.4	0.019		F(14)	C16F28O4H2	4	788.9451	2.3	24.9	
	SB(13)	C14F27O2H	1	712.9455	-2.4	31.4	0.004		F(15)	C17F30O4H2	4	838.9427	3.1	26.2	
	SB(14)	C15F29O2H	2	762.9434	-0.9	32.3		UPFAs	G(4)	C7F13OH	3	346.9732	-4.4	22.5	
	SB(15)	C16F31O2H	1	812.9405	-0.5	33.0	0.006		G(5)	C8F15OH	3	396.9709	-1.7	24.6	
	SB(16)	C17F33O2H	2	862.9365	-1.4	33.9			G(6)	C9F17OH	4	446.9663	-4.4	26.4	
	SB(17)	C18F35O2H	1	912.9323	-2.4	34.2	0.004		G(7)	C10F19OH	4	496.9664	2.6	27.8	
1:n PFECAs	A(8)	C10F19O3H	2	528.9528	-4.1	26.7			G(8)	C11F21OH	3	546.9615	-0.9	29.2	
	A(9)	C11F21O3H	2	578.9542	4.2	28.2			G(9)	C12F23OH	3	596.9597	1.5	30.4	
	A(10)	C12F23O3H	2	628.9487	0.3	29.4			G(10)	C13F25OH	3	646.9539	-2.5	31.3	
	A(11)	C13F25O3H	2	678.9451	-0.4	30.5			G(11)	C14F27OH	3	696.9513	-1.5	32.3	
	A(12)	C14F27O3H	2	728.9449	3.8	31.5			G(12)	C15F29OH	3	746.9494	0.4	33.1	
	A(13)	C15F29O3H	2	778.9392	0.2	32.4			G(13)	C16F31OH	3	796.9478	2.3	33.8	
	A(14)	C16F31O3H	4	828.9354	-0.5	33.1		OBS	H	C15H5F17SO4	2	602.9536	-4.7	26.8	
	A(15)	C17F33O3H	4	878.9318	-0.9	33.8		6:2 diPAP	I	C16H9F26O4P	1	788.9724	-3.4	31.3	0.014
n:2 FTAs	B(8)	C10F17O2H3	2	476.9777	-2.4	21.9		UPFCAs*	-	C9F15O2H	4	424.9645	-4.5	21.7	
	B(9)	C11F19O2H3	2	526.9746	-2.1	23.8			-	C10F17O2H	4	474.9622	-2.2	23.9	
	B(10)	C12F21O2H3	2	576.9727	0.4	25.6			-	C11F19O2H	4	524.9584	-3.1	25.7	
n:2 FTSs	C(6)	C8F13SO3H5	1	426.9667	-2.8	22.2	-0.042	Cl-PFCAs*	-	C8F14ClO2H	4	428.9355	-3.3	22.7	
	C(8)	C10F17SO3H5	1	526.9594	-4.1	26.3	-0.026		-	C9F16ClO2H	4	478.9345	1.7	24.9	
	C(10)	C12F21SO3H5	2	626.9521	-4.8	29.8			-	C10F18ClO2H	4	528.9293	-2.2	26.8	
H-PFdiOAs	D(8)	C11H3F17O4	4	520.9702	2.8	13.4			-	C11F20ClO2H	4	578.9251	-3.7	28.1	
	D(9)	C12H3F19O4	3	570.9644	-2.0	16.4			-	C12F22ClO2H	4	628.9242	0.2	29.5	
	D(10)	C13H3F21O4	3	620.9616	-1.1	18.8			-	C13F24ClO2H	4	678.9198	-1.7	30.6	



SA

PFSAs



SB

PFCAs

Figure S2. The identified PFASs with level 4 or above in APM. The letters in the "Proposed Structure" column refer to the generic structure represented by the same letters, and the numbers in parentheses in the "Proposed Structure" column indicate fluorinated chain length. The generic structure from A to I refer to the Figure 2 in manuscript.

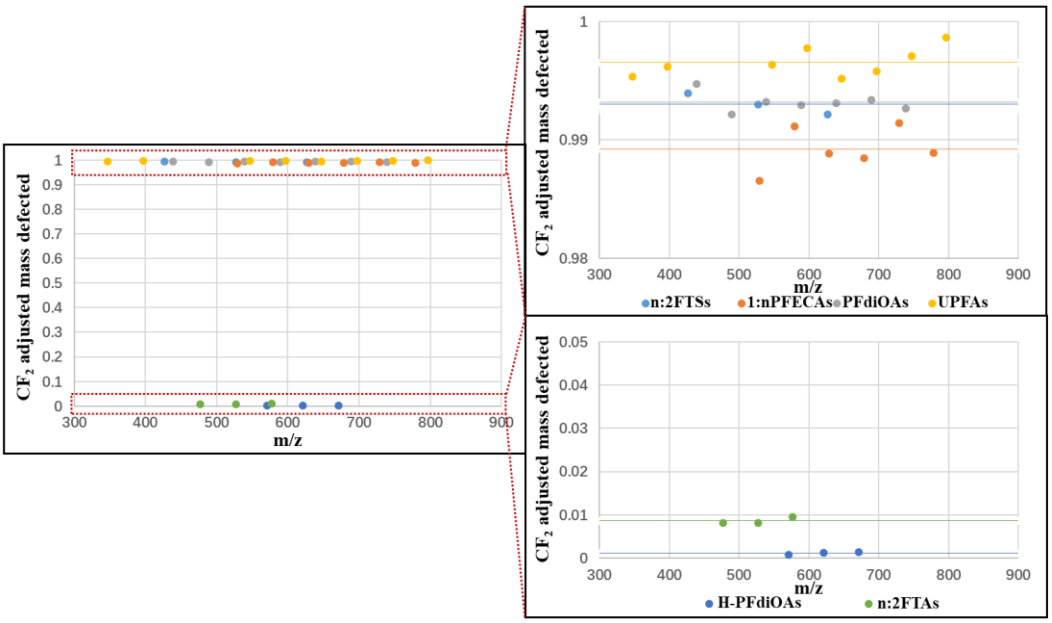


Figure S3 CF2 normalized adjusted Kendrick mass defect plot of identified PFASs (level 3 or above) by PFASs homologues analysis.

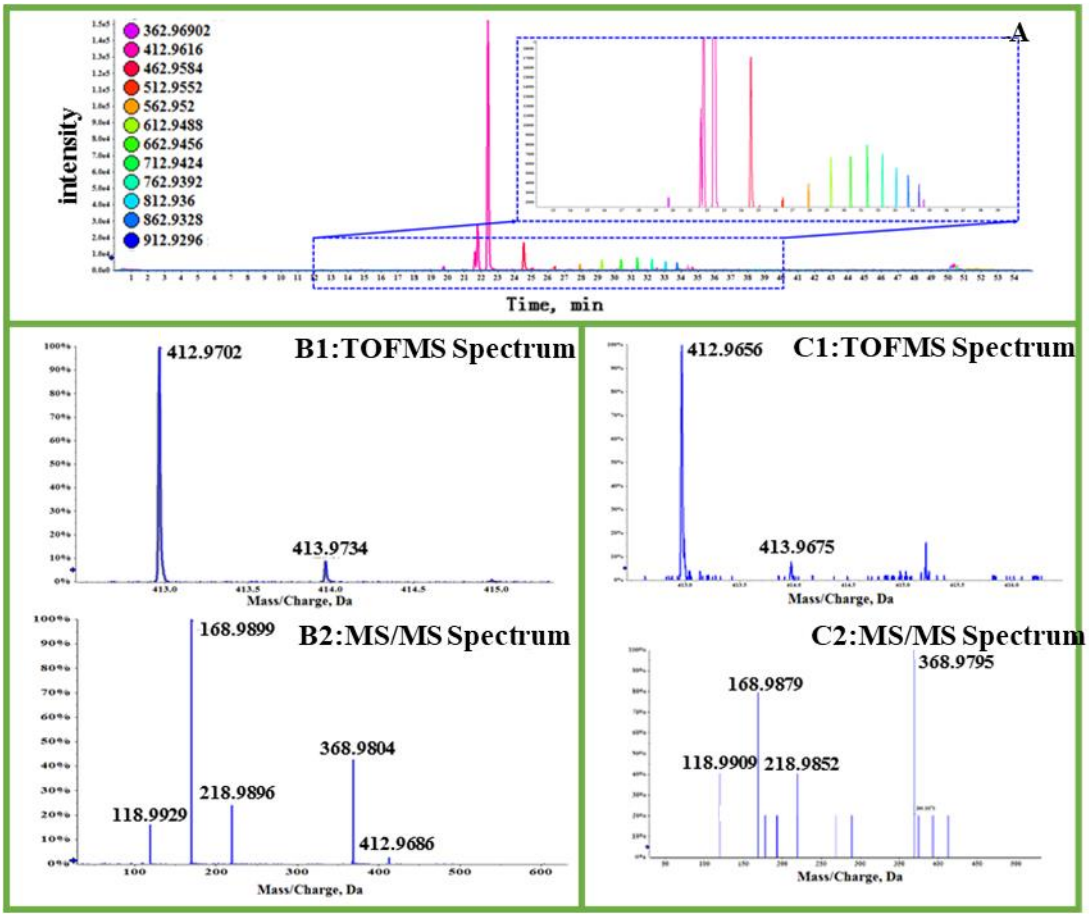


Figure S4. Identification of PFCAs using PFASs homologues analysis (A: EIC of identified PFCAs; B1: TOF-MS spectrum of PFOA in samples; B2: MS/MS spectrum of PFOA in samples; C1: TOF-MS spectrum of PFOA in standards; C2: MS/MS spectrum of PFOA in standards). By comparison with library spectra from AB sciex, the MS/MS match score was 99.3.

Fragment ion	Observe m/z	Error mDa	Error ppm	Confirm by Metfrag
$C_2F_5^-$	118.9940	1.4	12	Y
$C_3F_7^-$	168.9887	-0.7	-4.0	Y
$C_4F_9^-$	218.9858	-0.4	-1.7	Y
$C_5F_{11}^-$	268.9818	-1.2	-4.4	Y
$C_6F_{13}^-$	318.9824	2.6	8.2	
$C_7F_{15}^-$	368.9743	-2.3	-6.2	Y
$C_8F_{17}^-$	418.9770	3.6	8.6	
$C_9F_{19}^-$	468.9694	-0.8	-1.7	Y
$C_{10}F_{21}^-$	518.9597	-7.3	-14	
$C_{14}F_{29}^-$	718.9580	3.8	5.2	Y
$C_{15}F_{29}O_2^-$	762.9425	-1.6	-2.1	Y

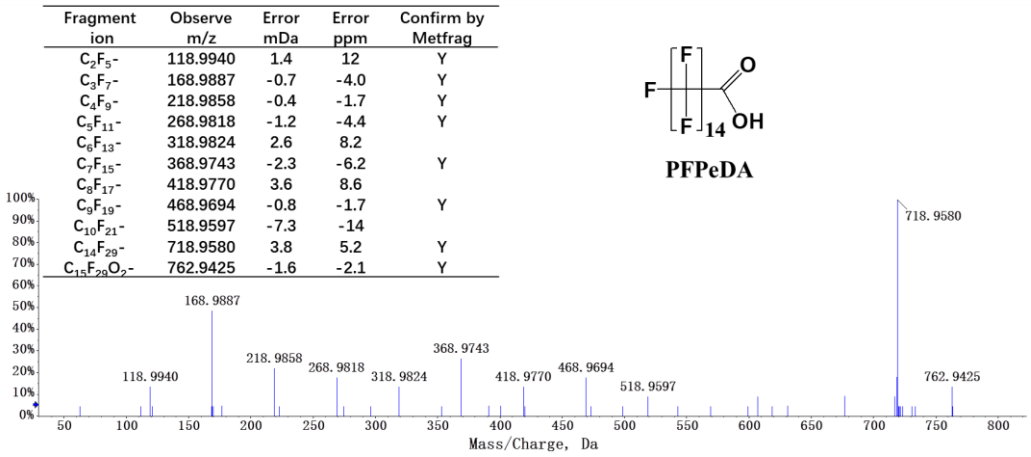


Figure S5. The MS/MS spectrum for PFPeDA. "Y" in the column of "Confirm by Metfrag" means that the fragment matches with the predicted fragment from Metfrag.

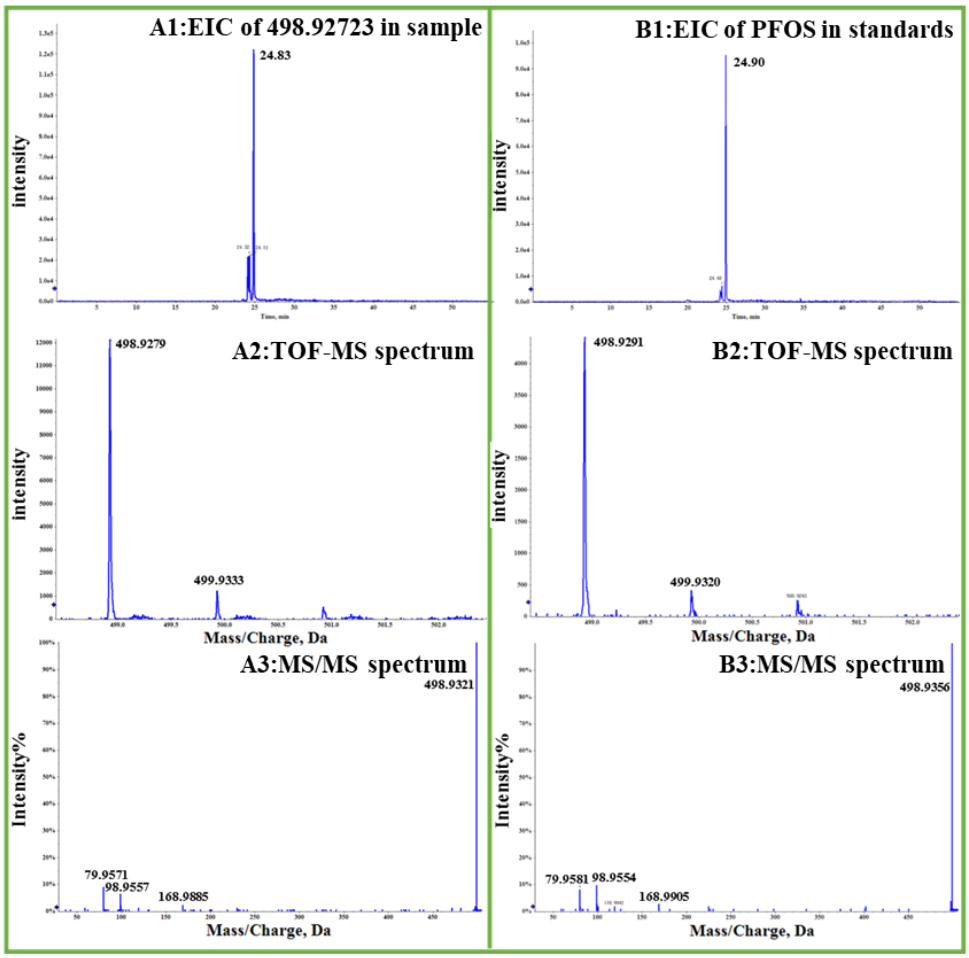
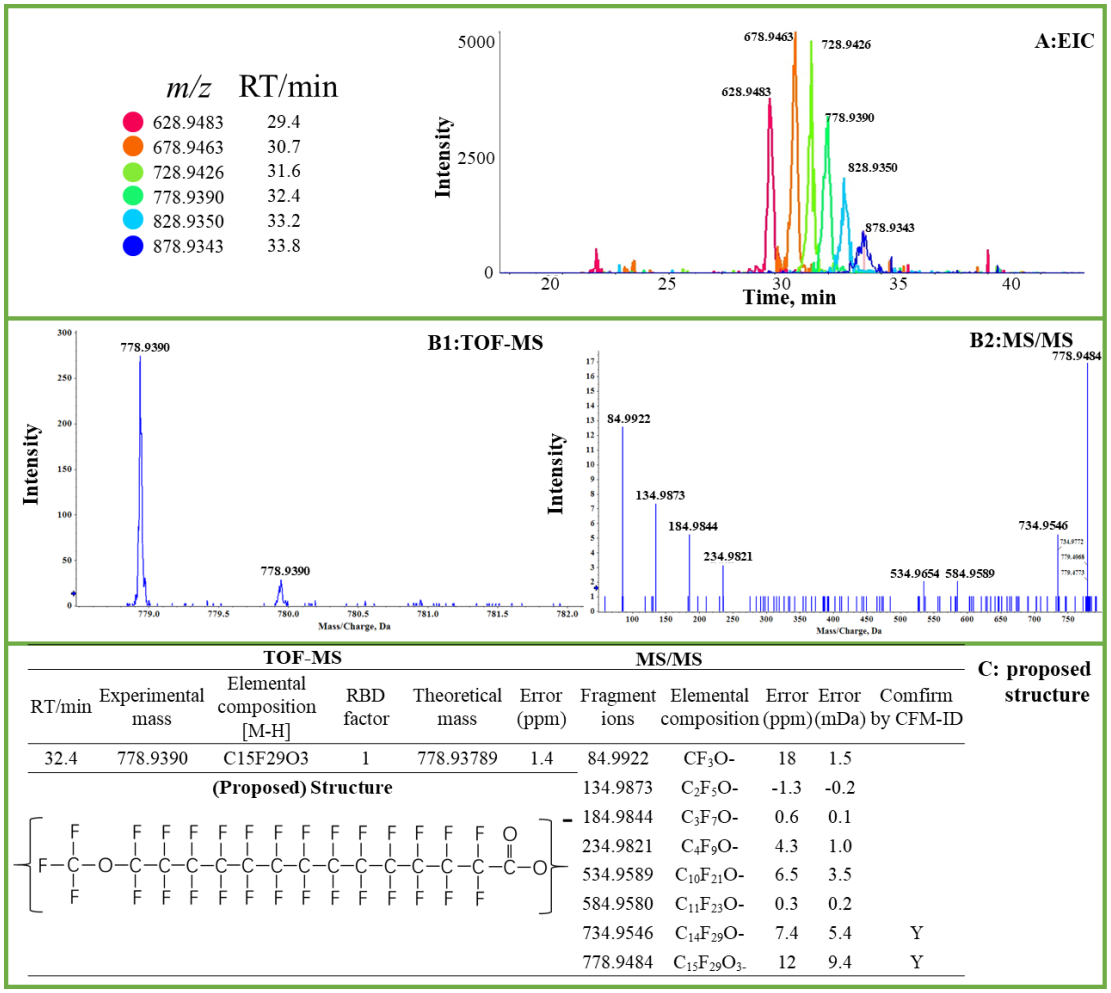


Figure S6. Identification of PFOS using PFASs homologues analysis (A1: EIC of 498.92723 in sample; A2: TOF-MS spectrum of 498.92723 in samples; A3: MS/MS spectrum of 498.92723 in samples; B1: EIC of PFOS; B2: TOF-MS spectrum of PFOS; B3: MS/MS spectrum of PFOS). By comparison with library spectra from AB sciex, the MS/MS match score was 96.3.

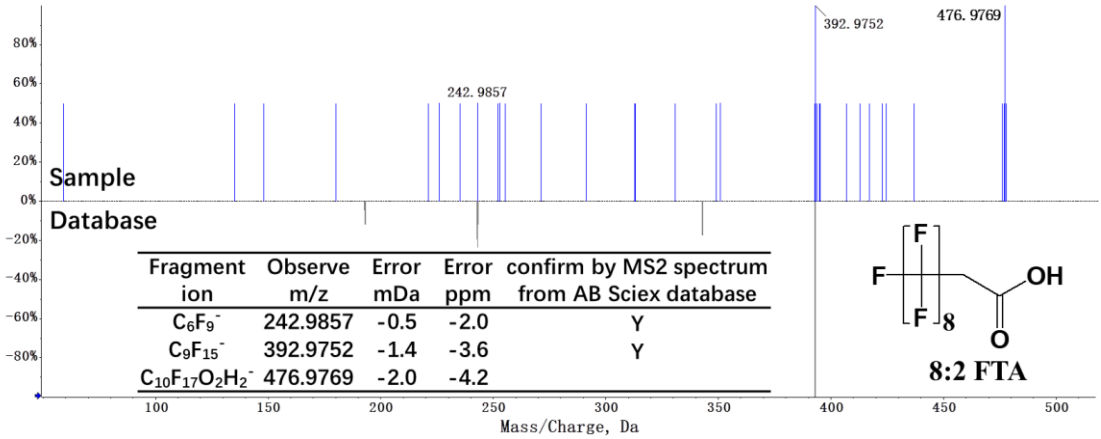


TOF-MS | **MS/MS** | **C: proposed structure**

RT/min	Experimental mass	Elemental composition [M-H]	RBD factor	Theoretical mass	Error (ppm)	Fragment ions	Elemental composition	Error (ppm)	Error (mDa)	Comfirm by CFM-ID
32.4	778.9390	C15F29O3	1	778.93789	1.4	84.9922	CF_3O-	18	1.5	
						134.9873	C_2F_5O-	-1.3	-0.2	
						184.9844	C_3F_7O-	0.6	0.1	
						234.9821	C_4F_9O-	4.3	1.0	
						534.9589	$C_{10}F_{21}O$-	6.5	3.5	
						584.9580	$C_{11}F_{23}O$-	0.3	0.2	
						734.9546	$C_{14}F_{29}O$-	7.4	5.4	Y
						778.9484	$C_{15}F_{29}O_3$-	12	9.4	Y

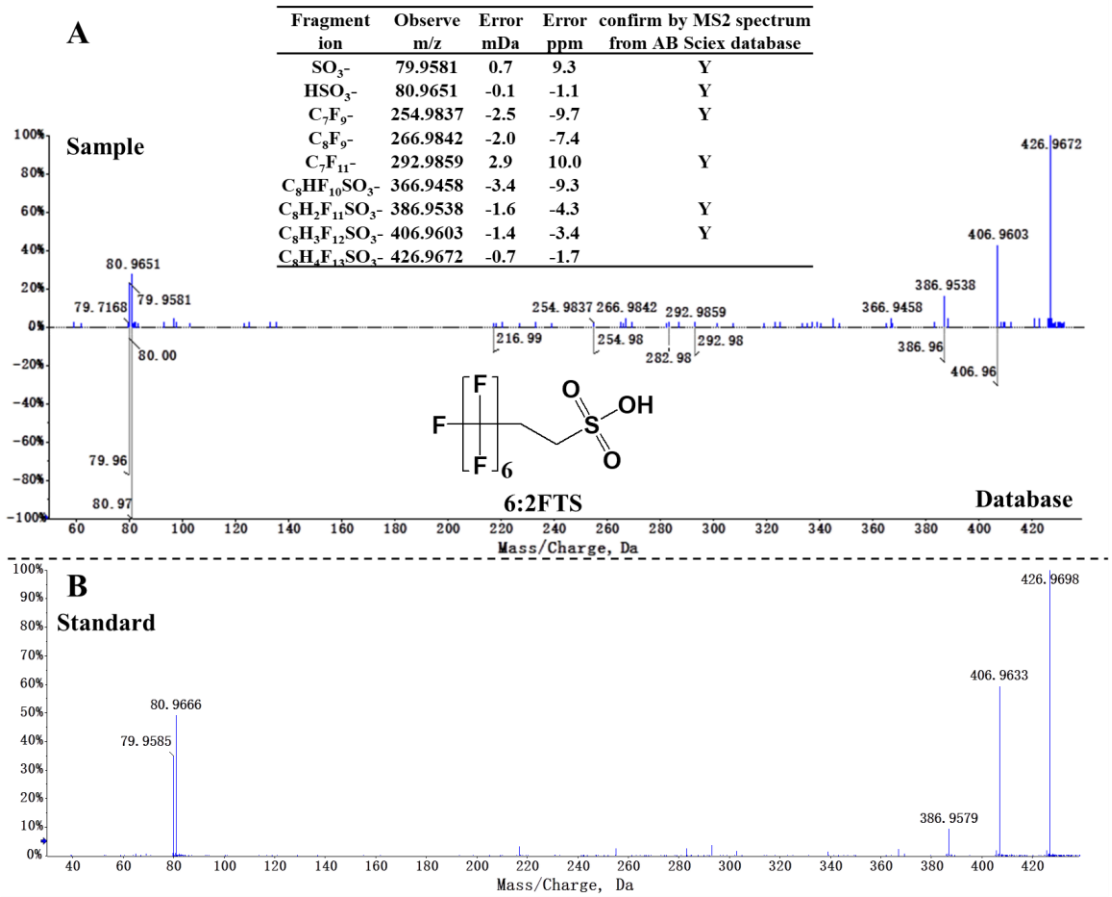
(Proposed) Structure

Figure S7. Identification of 1:n PFECAs: (A) EIC of the mass series of *m/z* 628.9,678.9,728.9,778.9,828.9,878.9; (B1) TOF-MS of *m/z* 778.9; (B2) MS/MS of *m/z* 778.9; and (C) the prososed structure. "Y" in the column of "Confirm by CFM-ID" means that the fragment matches with the predicted fragment from CFM-ID.



Fragment ion	Observe m/z	Error mDa	Error ppm	confirm by MS2 spectrum from AB Sciex database
$C_6F_9^-$	242.9857	-0.5	-2.0	Y
$C_9F_{15}^-$	392.9752	-1.4	-3.6	Y
$C_{10}F_{17}O_2H_2^-$	476.9769	-2.0	-4.2	

Figure S8. The MS/MS spectrum for 8:2 FTA. "Y" in the column of "Confirm by MS2 spectrum from AB Sciex database" means that the fragment matches with the fragment in the MS2 spectrum from AB Sciex database, and the MS/MS match score was 85.2.



Fragment ion	Observe m/z	Error mDa	Error ppm	confirm by MS2 spectrum from AB Sciex database
SO_3^-	79.9581	0.7	9.3	Y
HSO_3^-	80.9651	-0.1	-1.1	Y
$C_7F_9^-$	254.9837	-2.5	-9.7	Y
$C_8F_9^-$	266.9842	-2.0	-7.4	
$C_7F_{11}^-$	292.9859	2.9	10.0	Y
$C_8HF_{10}SO_3^-$	366.9458	-3.4	-9.3	
$C_8H_2F_{11}SO_3^-$	386.9538	-1.6	-4.3	Y
$C_8H_3F_{12}SO_3^-$	406.9603	-1.4	-3.4	Y
$C_8H_4F_{13}SO_3^-$	426.9672	-0.7	-1.7	

Figure S9. The MS/MS spectrum for 6:2 FTS. A: the comparison of MS/MS spectrum between sample and AB Sciex database. B: the MS/MS spectrum of 6:2 FTS standard. "Y" in the column of "Confirm by MS2 spectrum from AB Sciex database" means that the fragment matches with the fragment in the MS2 spectrum from AB Sciex database, and the MS/MS match score was for 67.2 between sample and AB Sciex database

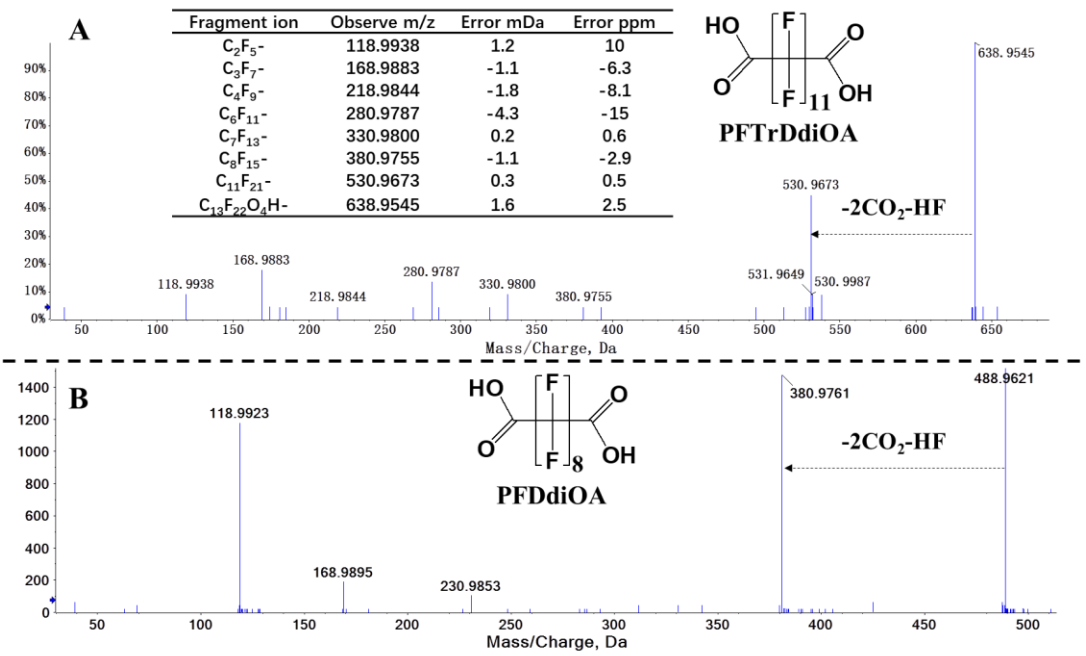


Figure S10. The MS/MS spectrum for PFTrDdiOA in sample (A) and PFDdiOA standard (B).

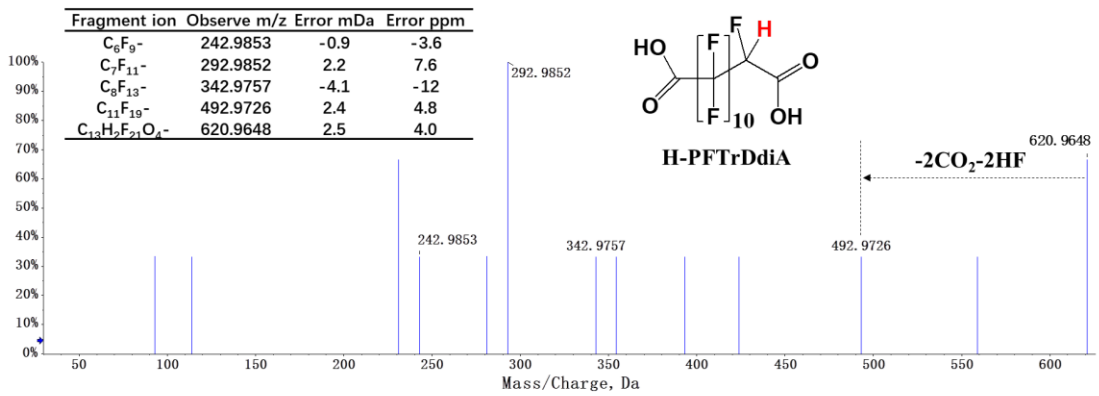


Figure S11. The MS/MS spectrum for H-PFTrDdiA.

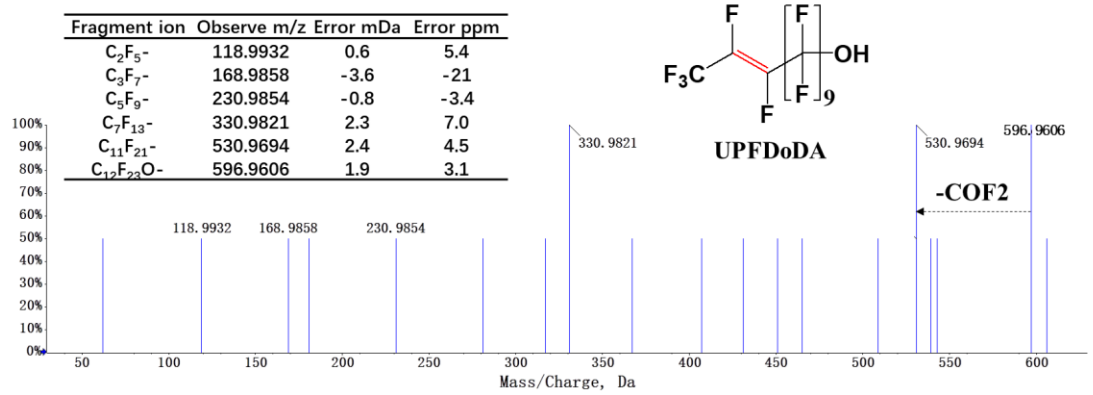


Figure S12. The MS/MS spectrum for UPFDoDA.

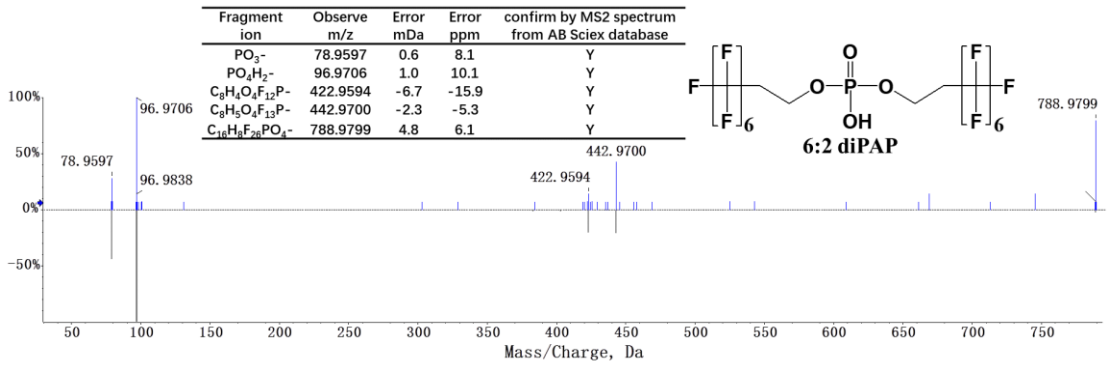


Figure S13. The MS/MS spectrum for 6:2 diPAP. "Y" in the column of "Confirm by MS2 spectrum from AB Sciex database" means that the fragment matches with the fragment in the MS2 spectrum from AB Sciex database, and the MS/MS match score was 83.8

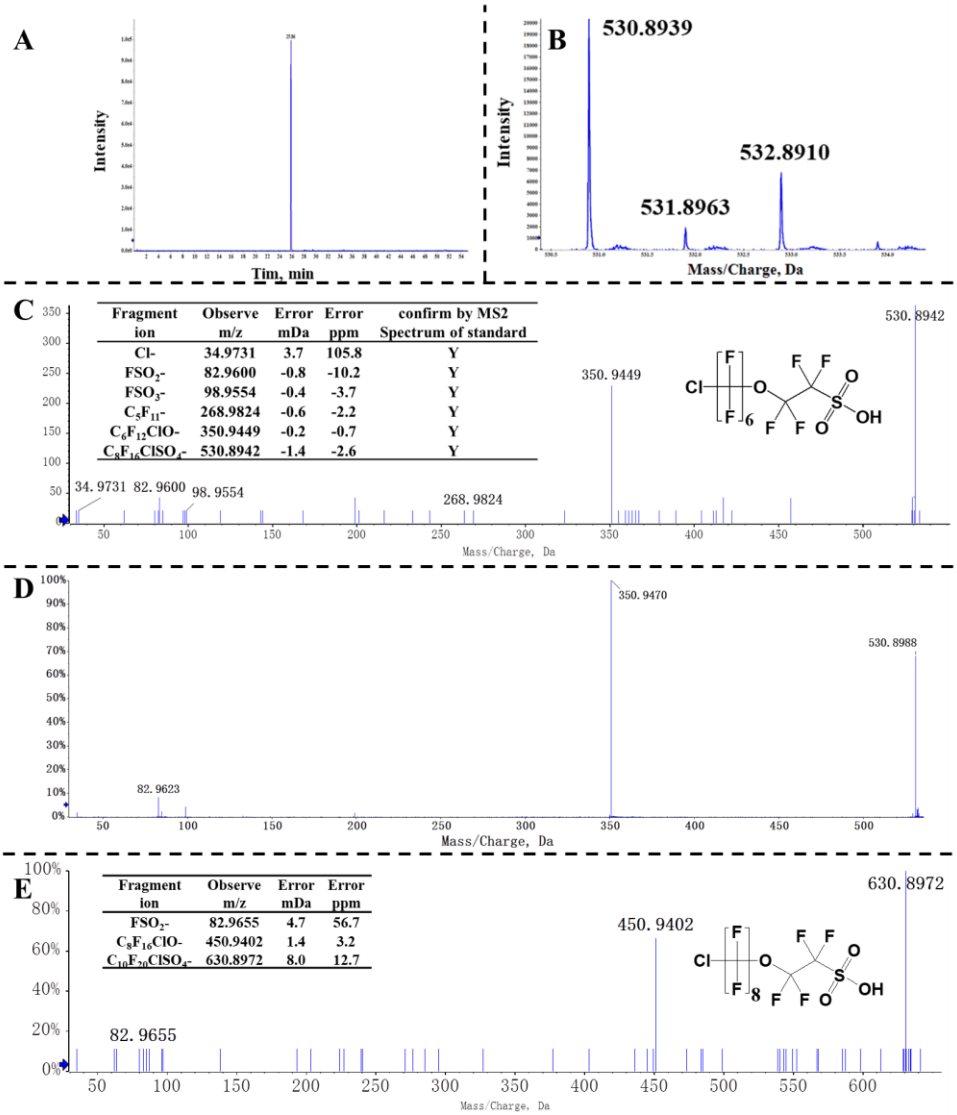
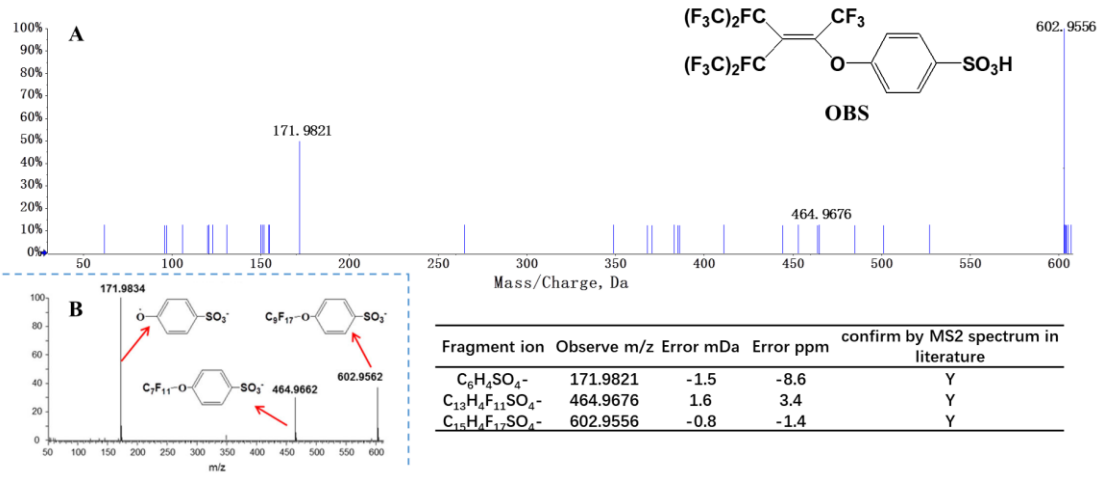


Figure S14. Identification of 6:2 Cl-PFESA. (A) EIC of 530.8988 in sample, (B) TOF-MS spectrum of 530.8988 in samples, (C) MS/MS spectrum of 530.8988 in samples, (D) MS/MS spectrum of 6:2 Cl-PFESA in standard, (E) MS/MS spectrum of 630.8880 in samples.



Fragment ion	Observe m/z	Error mDa	Error ppm	confirm by MS2 spectrum in literature
$C_6H_4SO_4$-	171.9821	-1.5	-8.6	Y
$C_{13}H_4F_{11}SO_4$-	464.9676	1.6	3.4	Y
$C_{15}H_4F_{17}SO_4$-	602.9556	-0.8	-1.4	Y

Figure S15. The MS/MS spectrum for OBS in sample (A) and literature[4] (B). "Y" in the column of "Confirm by MS2 spectrum in literature" means that the fragment matches with the fragment in the MS2 spectrum from literature.

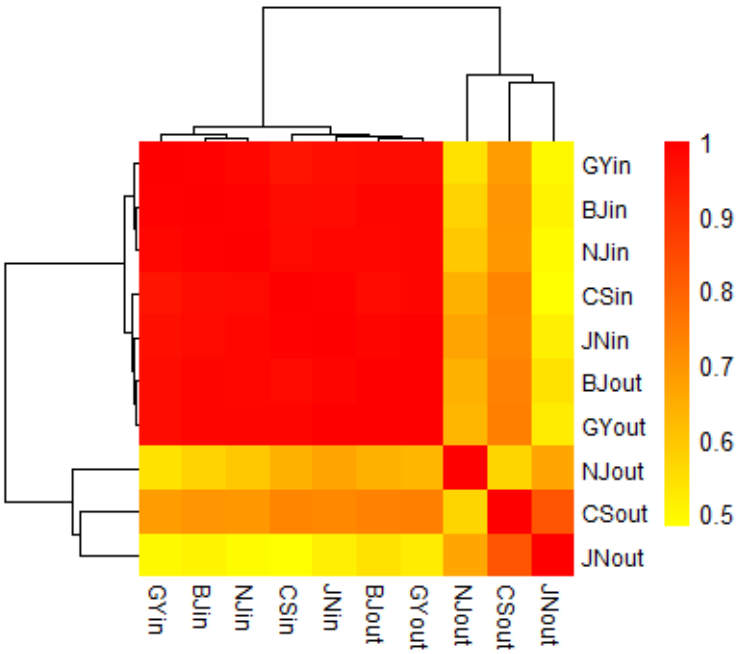


Figure S16. Correlation heatmap and hierarchical clustering of APM samples based on their Pearson correlation coefficients. "in" is for indoor, "out" is for outdoor. GY: Guiyang, BJ: Beijing, NJ: Nanjing, CS: Changshu, JN: Jinan.

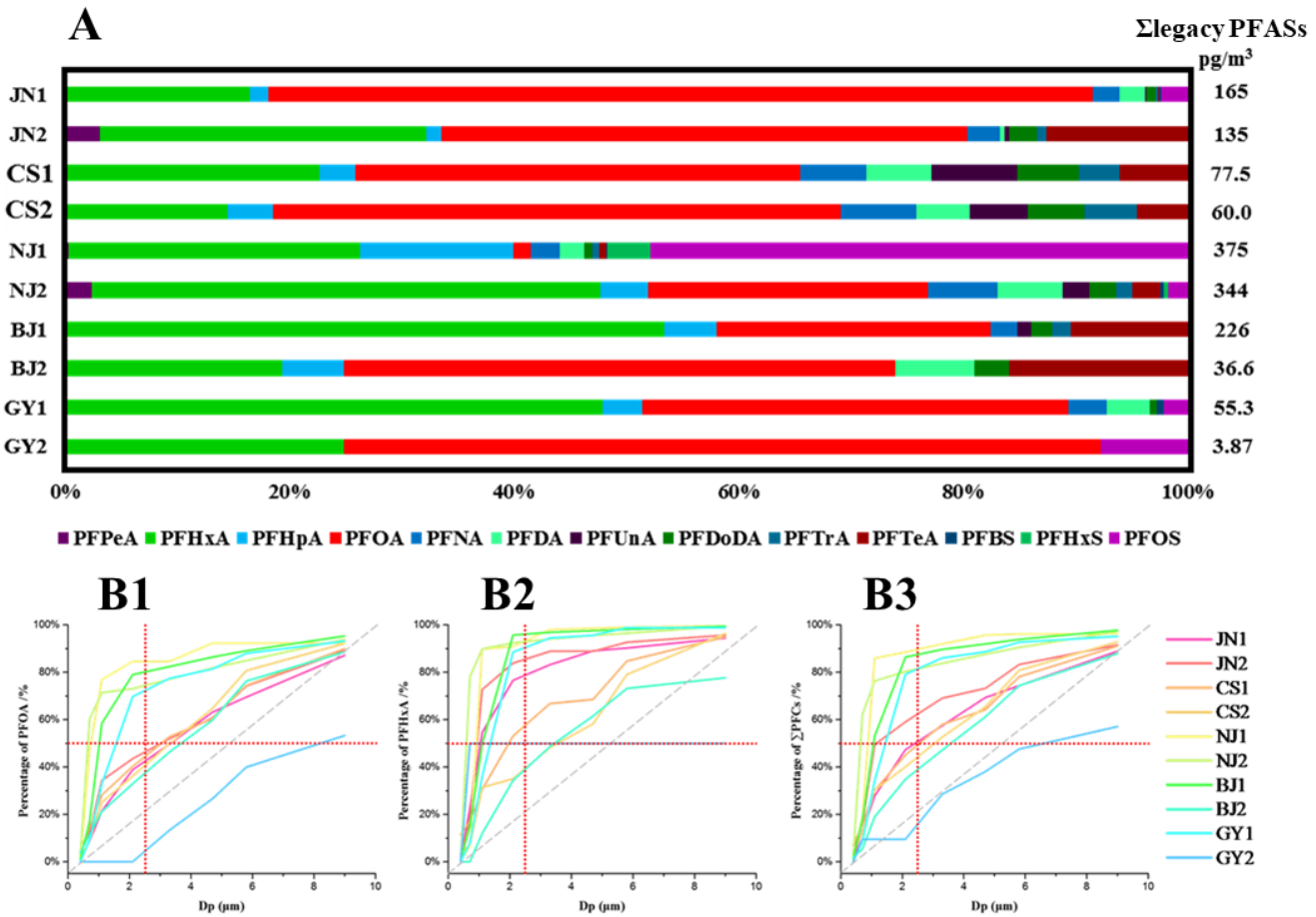


Figure S17. The proportional distribution and size distribution of legacy PFASs in indoor APM. A: proportional distribution of legacy PFASs in indoor APM; B: Size distribution of PFOA(B1), PFHxA(B2) and legacy PFASs(B3) in indoor APM. GY: Guiyang, BJ: Beijing, NJ: Nanjing, CS: Changshu, JN: Jinan.

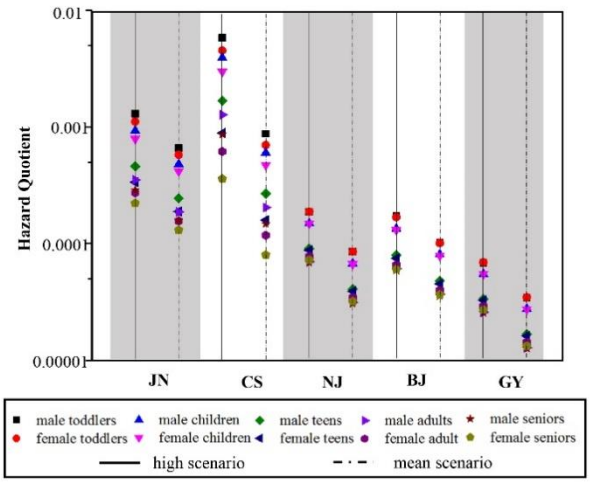


Figure S18. Age- and sex-specific health risks posed by PFOA via inhalation in urban China. GY: Guiyang, BJ: Beijing, NJ: Nanjing, CS: Changshu, JN: Jinan.

Table S4: sample information including name, location, sampling date and condition

Sample Number	longitude	latitude	Sampling Data		Condition
GY1	E106 °42' 18"	N26 °34' 27"	2014.6.30	2014.7.2	a
GY2	E106 °43' 7"	N26 °33' 50"	2014.7.3	2014.7.5	a
BJ1	E116 °18' 33"	N39 °58' 20"	2015.5.9	2015.5.11	a
BJ2	E116 °29' 11"	N39 °55' 31"	2015.5.12	2015.5.14	a
JN1	E117 °5' 15"	N36 °40' 43"	2014.11.20	2014.11.22	a
JNOUT2	E117 °1' 29"	N36 °40' 13"	2014.11.22	2014.11.23	b
JNIN2	E117 °1' 29"	N36 °40' 13"	2014.11.23	2014.11.25	b
NJOUT1	E118 °57' 36"	N32 °7' 23"	2014.2.20	2014.2.21	c#
NJOUT2	E118 °57' 36"	N32 °7' 23"	2014.2.21	2014.2.22	c#
NJOUT3	E118 °57' 36"	N32 °7' 23"	2014.2.22	2014.2.23	c#
NJOUT4	E118 °57' 36"	N32 °7' 23"	2014.3.09	2014.3.10	c#
NJOUT5	E118 °57' 36"	N32 °7' 23"	2014.3.10	2014.3.11	c#
NJOUT6	E118 °57' 36"	N32 °7' 23"	2014.4.29	2014.5.1	c
NJOUT7	E118 °57' 36"	N32 °7' 23"	2014.5.14	2014.5.16	c
NJOUT8	E118 °57' 36"	N32 °7' 23"	2014.5.19	2014.5.21	c
NJIN1	E118 °57' 41"	N32 °7' 4"	2014.4.13	2014.4.15	c
NJIN2	E118 °57' 41"	N32 °7' 4"	2014.4.16	2014.4.18	c
CSOUT1	E120 °47' 29"	N31 °48' 22"	2015.7.20	2015.7.22	c
CSOUT2	E120 °47' 29"	N31 °48' 22"	2015.7.22	2015.7.24	c
CSOUT3	E120 °47' 29"	N31 °48' 22"	2015.7.24	2015.7.26	c
CSOUT4	E120 °47' 29"	N31 °48' 22"	2015.7.26	2015.7.28	c
CSOUT5	E120 °47' 29"	N31 °48' 22"	2015.7.28	2015.7.30	c
CSOUT6	E120 °52' 37"	N31 °42' 44"	2015.7.20	2015.7.22	a
CSOUT7	E120 °45' 35"	N31 °40' 29"	2015.7.22	2015.7.24	b
CSOUT8	E120 °45' 50"	N31 °40' 29"	2015.7.24	2015.7.26	c
CSOUT9	E120 °45'12"	N31 °51'32"	2015.7.26	2015.7.28	c
CSOUT10	E120 °33'	N31 °53'56"	2015.7.28	2015.7.30	c
CSIN1	E120 °52' 37"	N31 °42' 44"	2015.7.20	2015.7.22	a
CSIN2	E120 °45' 35"	N31 °40' 29"	2015.7.23	2015.7.25	b

a: the indoor APM samples and outdoor APM samples were collected at same time and in or out a same residence; b: the indoor APM samples and outdoor APM samples were collected in or out a same residence but not at same time; c: the indoor APM samples and outdoor APM samples were collected neither at same time nor in or out a same residence.

Table S5: The sensitivity of HPLC-QTOF analysis with known PFASs standards at 0.1, 0.5, 1, and 0.5 µg L^{-1}, respectively

Analyte	Theoretical mass /Da	RT/min	0.1 µg L^{-1}		0.5 µg L^{-1}		1 µg L^{-1}		5 µg L^{-1}	
			Experimental mass/Da	Error/ ppm	Experimental mass/Da	Error /ppm	Experimental mass/Da	Error/ ppm	Experimental mass/Da	Error /ppm
PFPeA	262.976	9.32	-	-	-	-	-	-	262.97551	-1.9
PFHxA	312.9728	15.76	-	-	-	-	-	-	312.97372	2.91
PFHpA	362.9696	19.79	-	-	-	-	362.96802	-4.41	362.96933	-0.83
PFOA	412.9664	22.5	-	-	-	-	-	-	412.96559	-1.94
PFNA	462.9632	24.62	-	-	-	-	-	-	462.96231	-1.94
PFDA	512.96	26.37	-	-	-	-	-	-	512.9597	-0.58
PFUnA	562.9569	27.89	-	-	562.95498	-3.32	-	-	562.95654	-0.53
PFDoDA	612.9537	29.21	-	-	-	-	-	-	612.95449	1.37
PFTrA	662.9505	30.35	-	-	662.94762	-4.28	662.94721	-4.9	662.95044	0
PFTeA	712.9473	31.35	-	-	-	-	-	-	712.94619	-1.54
PFBS	298.943	13.01	-	-	-	-	298.94253	-1.54	298.94253	-1.67
PFHxS	398.9366	20.6	-	-	-	-	-	-	398.93568	-2.26
PFOS	498.9302	24.9	498.9284	-3.73	-	-	-	-	498.92948	-1.4
6:2diPAP	788.9751	31.31	-	-	788.9734	-2.1	788.97272	-2.97	788.97496	-0.13
8:2diPAP	988.9623	33.97	-	-	-	-	-	-	988.96443	2.17

Table S6: Parameters used in risk assessment

Generation and Gender	Age / year	Body Weight / kg	Daily Indoor Inhalation Rate / L^3 day^{-1}	Daily Outdoor Inhalation Rate / L^3 day^{-1}
male toddlers	0.5-4	15.7	6249	3587
female toddlers		15.3	6234	2696
male children	5-11	32.2	10337	4931
female children		32.0	10448	3701
male teens	12-19	67.5	13499	4375
female teens		60.6	12026	2018
male adults	20-59	86.8	13360	4272
female adult		74.7	13236	1698
male seniors	>60	84.1	12973	2766
female seniors		72.0	11932	904

Table S7: The CAS number, IUPAC name and SMILE for the identified PFASs with level 1 and level 2.

homologue	Formula	level	CAS	IUPAC name	SMILE
PFSAs	C4F9SO3H	1	375-73-5	1,1,2,2,3,3,4,4,4-Nonafluoro-1-butanesulfonic acid	C(C(C(F)(F)S(=O)(=O)O)(F)F)(C(F)(F)F)(F)F
	C6F13SO3H	1	355-46-4	1,1,2,2,3,3,4,4,5,5,6,6,6-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
	C8F17SO3H	1	1763-23-1	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-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
PFCAs	C6F11O2H	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
	C7F13O2H	1	375-85-9	2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptanoic acid	C(=O)(C(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)O
	C8F15O2H	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
	C9F17O2H	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(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)O
	C10F19O2H	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)O
	C11F21O2H	1	2058-94-8	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-henicosafluoroundecanoic acid	C(=O)(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)O
	C12F23O2H	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)O
	C13F25O2H	1	72629-94-8	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-pentacosafluorotridecanoic acid	C(=O)(C(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)O
	C14F27O2H	1	376-06-7	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptacosafluorotetradecanoic acid	C(=O)(C(C(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)O
	C15F29O2H	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,15-nonacosafluoropentadecanoic acid	C(=O)(C(C(C(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

homologue	Formula	level	CAS	IUPAC name	SMILE
PFCAs	C16F31O2H	1	67905-19-5	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-hentriacontafluorohexadecanoic acid	C(=O)(C(C(C(C(C(C(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)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)O
	C17F33O2H	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-tritriacontafluoroheptadecanoic acid	C(=O)(C(C(C(C(C(C(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)(F)F)(F)F)(F)F)(F)F)(F)F)O
	C18F35O2H	1	16517-11-6	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-pentatriacontafluorooctadecanoic acid	C(=O)(C(C(C(C(C(C(C(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)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)O
1:n PFECAs	C10F19O3H	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-9-(trifluoromethoxy)nonanoic acid	C(OC(C(C(C(C(C(C(C(C(=O)O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F
	C11F21O3H	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-octadecafluoro-10-(trifluoromethoxy)decanoic acid	C(OC(C(C(C(C(C(C(C(C(C(O)=O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F
	C12F23O3H	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-icosafluoro-11-(trifluoromethoxy)undecanoic acid	C(OC(C(C(C(C(C(C(C(C(C(=O)O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F
	C13F25O3H	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-docosafluoro-12-(trifluoromethoxy)dodecanoic acid	C(OC(C(C(C(C(C(C(C(C(C(C(O)=O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F
	C14F27O3H	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13-tetracosafluoro-13-(trifluoromethoxy)tridecanoic acid	C(OC(C(C(C(C(C(C(C(C(C(C(C(C(O)=O)(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
	C15F29O3H	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-hexacosafluoro-14-(trifluoromethoxy)tetradecanoic acid	C(OC(C(C(C(C(C(C(C(C(C(C(C(C(C(O)=O)(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)F
n:2 FTAs	C10F17O2H3	2	27854-31-5	3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecanoic acid	C(C(C(C(C(C(C(C(C(CC(=O)O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F
	C11F19O2H3	2		3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Nonadecafluoroundecanoic acid	C(C(C(C(C(C(C(C(C(CC(=O)O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F
	C12F21O2H3	2	53826-13-4	3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Henicosafluorododecanoic acid	C(C(C(C(C(C(C(C(C(CC(=O)O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F

homologue	Formula	level	CAS	IUPAC name	SMILE
n:2 FTSs	C8F13SO3H5	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
	C10F17SO3H5	1	39108-34-4	3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecane-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)C(F)(F)C(F)(F)F
	C12F21SO3H5	2	120226-60-0	3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Henicosafluoro-1-dodecanesulfonic acid	C(CS(=O)(=O)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
PFdiOAs	C9F14O4H2	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8-tetradecafluorononanedioic acid	C(C(C(C(C(C(C(C(C(C(=O)O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(=O)O
	C10F16O4H2	1	307-78-8	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorodecanedioic acid	C(=O)(C(C(C(C(C(C(C(C(C(C(=O)O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)O
	C11F18O4H2	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-octadecafluoroundecanedioic acid	C(C(C(C(C(C(C(C(C(C(C(O)=O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(=O)O
	C12F20O4H2	1	865-85-0	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-icosafluorododecanedioic acid	C(=O)(C(C(C(C(C(C(C(C(C(C(C(=O)O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)O
	C13F22O4H2	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-docosafluorotridecanedioic acid	C(C(C(C(C(C(C(C(C(C(C(C(=O)O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(O)=O
	C14F24O4H2	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13-tetracosafluorotetradecanedioic acid	C(C(C(C(C(C(C(C(C(C(C(C(C(O)=O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(=O)O
	C15F26O4H2	2		2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-hexacosafluoropentadecanedioic acid	C(C(C(C(C(C(C(C(C(C(C(C(C(C(O)=O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(=O)O
6:2 diPAP	C16H9F26O4P	1	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)C(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F
n:2 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
	C10HClF20O4S	2		2-(8-chloro-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hexadecafluoro-octoxy)-1,1,2,2-tetrafluoro-ethanesulfonic acid	C(C(C(C(C(F)(F)Cl)(F)F)(F)F)(F)F)(C(C(C(OC(C(F)(F)S(=O)(=O)O)(F)F)(F)F)(F)F)(F)F)(F)F

homologue	Formula	level	CAS	IUPAC name	SMILE
OBS	C15H5F17SO4	2	271794-15-1	4-{[1,1,1,4,5,5,5-heptafluoro-3-(1,1,1,2,3,3,3-heptafluoropropan-2-yl)-4-(trifluoromethyl)pent-2-en-2-yl]oxy}benzene-1-sulfonic acid	C(=C(C(F)(F)F)OC1=CC=C(C=C1)[S](=O)(=O)O)(C(C(F)(F)F)(C(F)(F)F)F)C(C(F)(F)F)(C(F)(F)F)F

Table S8: The detection in APM for the identified PFASs with level 4 and level 5.

Homologue	Formula	level	Observe m/z	RT min	Detection in APM		Homologue	Formula	level	Observe m/z	RT min	Detection in APM	
					Indoor	Outdoor						Indoor	Outdoor
PFSAs	C7F15SO3H	4	448.9331	22.9	BJ;CS;GY;NJ	BJ;CS;GY;NJ	Class 8		5	298.0815	7.5		NJ
1:n PFECAs	C16F31O3H	4	828.9354	33.1		CS			5	348.0779	11.6		NJ
	C17F33O3H	4	878.9318	33.8		CS			5	398.0746	12.4		JN;NJ
H-PFdiOAs	C11H3F17O4	4	520.9702	13.4		JN	Class 9		5	299.1131	13.4		NJ
	C15H3F25O4	4	720.9546	22.5	CS;GY	CS;GY			5	349.1084	20.5		NJ
PFdiOAs	C16F28O4H2	4	788.9451	24.9	GY;JN	CS			5	399.1057	24.5		JN;NJ
	C17F30O4H2	4	838.9427	26.2		GY	Class 10		5	301.0944	8.6	GY	
UPFAs	C9F17OH	4	446.9663	26.4		CS			5	351.0919	12.0		JN
	C10F19OH	4	496.9664	27.8		CS;GY			5	401.0896	14.5		JN;NJ
UPFCAs*	C9F15O2H	4	424.9645	21.7	BJ;GY;NJ	BJ;CS;GY	Class 11		5	301.1259	10.5		NJ
	C10F17O2H	4	474.9622	23.9	BJ;CS;GY;JN;NJ	BJ;CS;GY;NJ			5	351.1227	19.9		JN
	C11F19O2H	4	524.9584	25.7	BJ;GY;JN;NJ	BJ;CS;GY;NJ			5	401.1206	27.5		JN
Cl-PFCAs*	C8F14ClO2H	4	428.9355	22.7		CS	Class 12		5	302.0694	9.9		NJ
	C9F16ClO2H	4	478.9345	24.9		CS			5	352.0682	11.0		CS;JN;NJ
	C10F18ClO2H	4	528.9293	26.8		CS			5	402.0643	12.5		NJ
	C11F20ClO2H	4	578.9251	28.1	JN	CS	Class 13		5	309.1141	11.1		JN
	C12F22ClO2H	4	628.9242	29.5		CS			5	359.1118	17.1		JN
	C13F24ClO2H	4	678.9198	30.6	CS	CS			5	409.1081	21.3		JN
Class 1		5	169.0868	8.5	BJ	BJ;CS;GY;JN;NJ	Class 14		5	317.0860	4.8		NJ
		5	269.0819	13.8		JN			5	367.0812	11.5		JN
		5	369.0746	15.0		NJ			5	417.0799	15.7		JN

Homologue	Formula	level	Observe m/z	RT min	Detection in APM		Homologue	Formula	level	Observe m/z	RT min	Detection in APM	
					Indoor	Outdoor						Indoor	Outdoor
Class 2		5	197.0826	7.9		NJ	Class 15		5	325.0959	6.5		CS;GY
		5	247.0793	11.8		NJ			5	375.0929	11.6		JN;NJ
		5	297.0755	12.4		CS;JN;NJ			5	425.0876	17.0		NJ
Class 3		5	229.1092	7.7		NJ	Class 16		5	327.0724	6.0		JN;NJ
		5	279.1069	14.7		NJ			5	377.0687	10.9		BJ
		5	329.1043	18.1		JN			5	427.0663	12.6		JN;NJ
Class 4		5	260.0594	5.0		CS	Class 17		5	331.0859	6.0		NJ
		5	310.0575	7.0		JN			5	381.0826	8.5		JN
		5	360.0530	7.7		JN;NJ			5	431.0792	9.8		NJ
Class 5		5	275.0560	8.2		JN;NJ	Class 18		5	355.1036	7.7		JN
		5	325.0534	10.1		NJ			5	405.1016	13.8		JN
		5	375.0481	11.9		GY			5	455.0987	21.6		CS
Class 6		5	280.1031	10.9		BJ	Class 19		5	385.1124	7.3		JN
		5	330.1008	13.0		JN;NJ			5	435.1100	13.1		JN
		5	380.0958	14.3		CS;GY;JN			5	485.1067	20.4		NJ
Class 7		5	283.1017	16.5		JN							
		5	333.0971	17.1		CS;JN;NJ							
		5	383.0947	17.6		JN;NJ							

Table S9: Levels of PFCAs, PFSAs and 6:2diPAP (pg m^{-3}) measured in outdoor air particle in five cities in China.

	JN (n=2)		CS (n=10)		NJ (n=8)		BJ (n=2)		GY (n=2)	
	mean	**maximum**	**mean**	**maximum**	**mean**	**maximum**	**mean**	**maximum**	**mean**	**maximum**
PFPeA	12.9	23.0	6.85	26.4	0.85	2.70	0.51	0.53	ND	ND
PFHxA	31.5	57.5	23.2	48.3	1.10	2.64	1.34	1.58	1.31	1.75
PFHpA	9.25	11.2	11.7	50.0	0.51	0.79	0.99	1.40	0.24	0.38
PFOA	325	544	556	3515	11.6	24.8	12.5	18.8	2.07	2.51
PFNA	2.78	4.20	12.8	101	0.65	1.03	0.17	0.17	0.58	0.60
PFDA	4.82	7.65	15.6	129	0.72	0.98	0.32	0.33	0.42	0.45
PFUnA	1.66	2.73	19.3	161	0.70	1.04	0.42	0.62	0.50	0.58
PFDoDA	4.79	8.87	19.4	160	0.50	0.57	0.56	0.70	0.15	0.20
PFTrA	2.19	3.72	19.8	161	0.56	0.94	0.41	0.59	0.19	0.20
PFTeA	13.7	26.9	18.8	153	0.53	0.99	2.48	3.63	ND	ND
PFBS	0.49	0.97	0.96	2.49	0.73	3.42	ND	ND	0.04	0.09
PFHxS	0.11	0.22	1.83	3.63	2.01	4.39	ND	ND	ND	ND
PFOS	6.28	6.43	8.37	15.6	4.30	10.6	0.80	1.24	0.14	0.19
6:2diPAP	0.15	0.29	3.37	6.00	1.82	3.31	0.60	0.85	ND	ND

Table S10: The identified PFASs in ESI positive mode.

Homologue	level	Observe m/z	RT min	Detection in APM	
				Indoor	Outdoor
Class 1+	5	235.0596	1.9		NJ
	5	285.0571	6.9		NJ
	5	335.0520	14.3	NJ	BJ;CS;GY;JN;NJ
Class 2+	5	197.1168	17.0		BJ;GY;JN;NJ
	5	247.1141	21.9		CS;GY;JN
	5	297.1088	22.2		CS;GY;JN;NJ
Class 3+	5	252.1236	14.5	JN	
	5	302.1208	17.5	BJ	BJ;CS;GY
	5	352.1166	20.4	NJ	CS;GY
Class 4+	5	233.1140	16.5	BJ;CS;GY;JN;NJ	
	5	333.1082	22.0	BJ;CS;GY	BJ;CS;GY;NJ
	5	433.1022	25.1	BJ;CS	CS
Class 5+	5	161.1315	16.6	BJ;CS;GY;JN	
	5	211.1293	17.7	JN	GY
	5	261.1258	25.6	BJ;GY;JN;NJ	BJ

Reference

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