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Article

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

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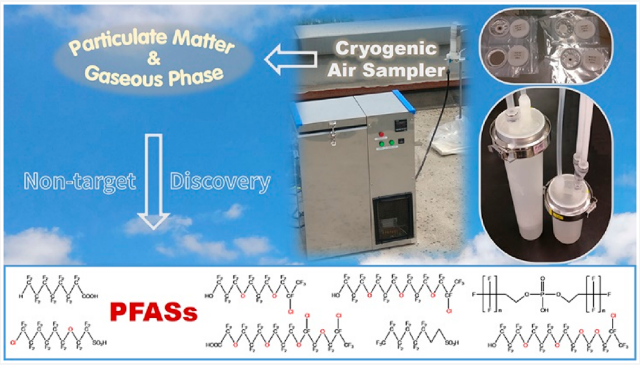
ABSTRACT: Novel per- and polyfluoroalkyl substances (PFASs) have become a key issue in global environmental studies. Although several novel PFASs have been discovered in atmospheric particulate matter through nontarget analysis, information on the environmental occurrence of novel PFASs in atmospheric gaseous phases and conventional sampling techniques is somewhat deficient. Therefore, this Article describes a new type of air sampler, the cryogenic air sampler (CAS), which was used to collect all atmospheric components simultaneously. Nontarget analysis then was performed through PFASs homologue analysis. A total of 117 PFAS homologues (38 classes) were discovered, 48 of which (13 classes) were identified with confidence Level 4 or above. Eleven chlorinated perfluoropolyether alcohols (3 classes) and four chlorinated perfluoropolyether carboxylic acids (2 classes) have been reported for the first time in this Article. This Article is also the first report of 12 hydrosubstituted perfluoroalkyl carboxylates (H-PFCAs) in the atmosphere. H-PFCAs and chlorinated perfluoropolyether carboxylic acids were mainly distributed in the particular phase. These results are evidence that novel chlorinated polyether PFASs should be the focus of future study.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) have been widely used worldwide since the 1930s due to their unique ability to repel both grease and water.[1] PFASs are found everywhere in modern industry and in products such as fire-fighting foam, food contact materials, cosmetics, mining, textiles, and household products.[2] Perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA), representative examples of PFASs, have been proven to be environmentally persistent and biotoxic[3,4] and are listed in the Stockholm Convention as persistent organic pollutants (POPs).[5,6] Although PFOS and PFOA have been phased out and banned in numerous countries around the world, the increased use of different alternatives to PFOS and PFOA has grown the PFASs family, and as of last year 4730 PFASs were cited in different patents or registered as chemicals;[1] there are currently more than 5000 PFASs in various lists[7] on the U.S. EPA CompTox Chemistry Dashboard. At the same time, a variety of PFASs have been detected in the environment,[8] including air, water, sediments, soil, sludge, dust, wildlife, and even the human body.[9] Persistence and long-range mobility have allowed PFASs to even appear in the polar atmosphere.[10] Although some alternatives such as perfluorohexanoic acid (PFHxA) have been shown to be less toxic than PFOA and PFOS,[11,12] there are still many novel PFASs that are indicated to have stronger bioaccumulation and biotoxicity, such as chlorinated polyfluorinated ether sulfonate (Cl-PFESA, commercial name: F-53B) as an alternative to PFOS[13−17] and hexafluoropropylene oxide trimer acid (HFPO-TA) as an alternative to PFOA.[18−20] However, there is no effective control over these novel PFASs, and they require greater attention as environmental hazards.

Because the chemical industry treats these emerging alternatives as trade secrets without publishing precise structures, and a large number of transformation products are formed by abiotic or/and biotic processes in the environment, researchers are faced with a large number of PFASs with unknown structures.[1] Qualitative and quantitative organic fluorides constitute only a very limited part of the total organic fluorine present in the environment.[21] Facing numerous unknown novel PFASs, nontarget analysis strategies

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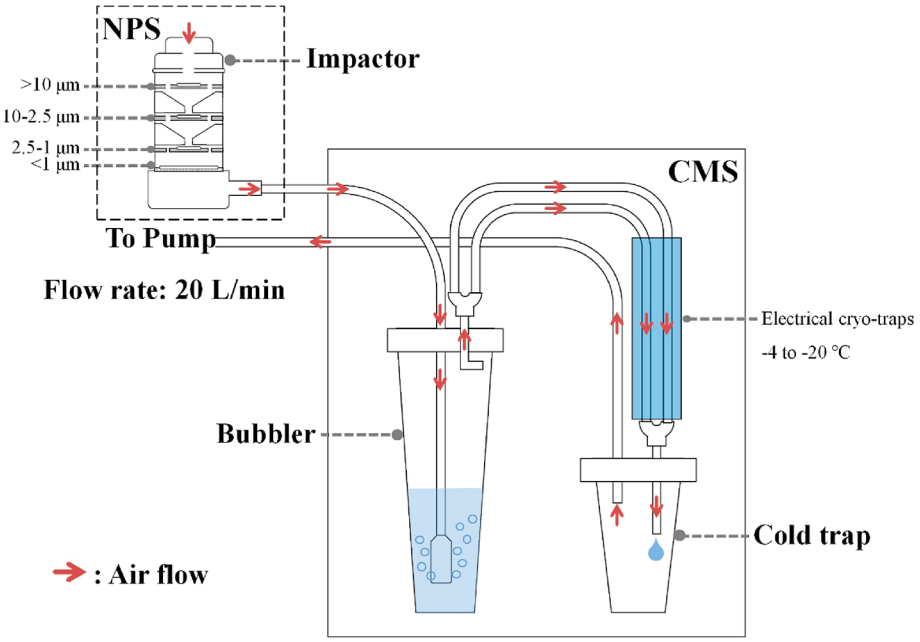

Figure 1. Schematic diagram of the cryogenic air sampler.

based on high-resolution mass spectrometry (HRMS) have become a primary means of detecting and identifying them.[22−25] Since 2010, nontarget analysis with HRMS has been used in various environmental media such as water,[26−31] atmospheric particulate matter,[32] soil[33] and sediment[30] to detect novel PFASs; more than 750 PFASs belonging to more than 130 diverse classes have been discovered through nontarget analytical methods.[7]

Some studies have reported the distribution of PFASs in the particle and gaseous phase of the atmosphere,[34−40] indicating that the concentration of PFASs in the global atmosphere is increasing year after year,[34] and that ionizable PFASs show stronger affinity to atmospheric particulate matter than do neutral PFASs.[36,38] However, the existing studies only focus on legacy PFASs such as perfluoroalkyl carboxylates (PFCAs), perfluoroalkyl sulfonates (PFSAs), fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs), and perfluorooctane sulfonamidoethanols (FOSEs) without studying the distribution of novel PFASs in air, especially the gaseous phase of air. Furthermore, traditional air samplers primarily use adsorbent materials such as polyurethane foam (PUF) for specific pollutants, which can only guarantee the absorption performance of the target PFASs.[41−43] It is difficult to collect pollutants effectively from high-humidity air using PUF.[44] On the other hand, the usage of adsorbent materials will induce significant artifactual responses,[45] which is not suitable for nontarget analysis. In addition, there are few single samplers for sampling both particle and gaseous phase in air simultaneously.[46] Therefore, there is a need for a suitable sampler for the comprehensive study of unknown novel PFASs in air, including from the particulate matter and gaseous phase.

With these issues in mind, we used a new type of air sampler, the cryogenic air sampler (CAS), to collect both the atmospheric particulate matter and the gaseous phase comprehensively at the same time. Novel PFASs in air were screened and identified by a nontarget strategy of PFAS homologue analysis, and the distributions of the screened novel PFASs were characterized between the particulate matter and the gaseous phases of the atmosphere.

■ MATERIALS AND METHODS

Cryogenic Air Sampler. This new kind of all-component air sampler developed by the National Institute of Advanced Industrial Science and Technology (AIST) and Sibata Scientific Technology Ltd.[44,46] is composed primarily of a cryogenic moisture sampler (CMS) and a nanoparticle sampler (NPS), which, respectively, collect gaseous and particulate samples (Figure 1). Two components are used in series during the sampling process. Air first passes the NPS, which is a cascade impactor, and particles are separately collected by the impactor according to different size ranges (>10 μm, 10−2.5 μm, 2.5−1.0 μm, and <1.0 μm). After that, air without particulate matter enters the CMS, which is composed of a bubbler and a cold trap. The components in the air are first absorbed by the solution in the bubbler and then are collected in a cold trap, which uses an electrical cryo-trap. Using cryogenic collection of air, CMS can collect all types of high- and low-boiling gaseous chemicals including very volatile organic compounds, volatile organic compounds, and semi-volatile organic compounds, which depended on the temperature set for the cold trap. The impactor of the NPS as well as the tubes and containers of CMS are made of polypropylene to avoid adsorption onto glass surfaces. For PFASs sampling, considering the solubility of PFASs, 10% methanol aqueous solution is chosen as the absorption solution in the bubbler. The cold trap then collects all moisture (as ice) and adsorption solvent using electrical cryo-traps at −10 °C. CAS has demonstrated a high recovery (>80%) of PFCAs (C4−C11) and PFSAs (C4−C8) in all-component air.[44]

Chemicals. Complete information on the authentic standards and reagents used in this study is listed in Supporting Information section 1. All solvents and reagents used were high-performance liquid chromatography (HPLC) grade.

Sample Collection. Four samples were collected at the top of a building in Nanjing University, Nanjing, China

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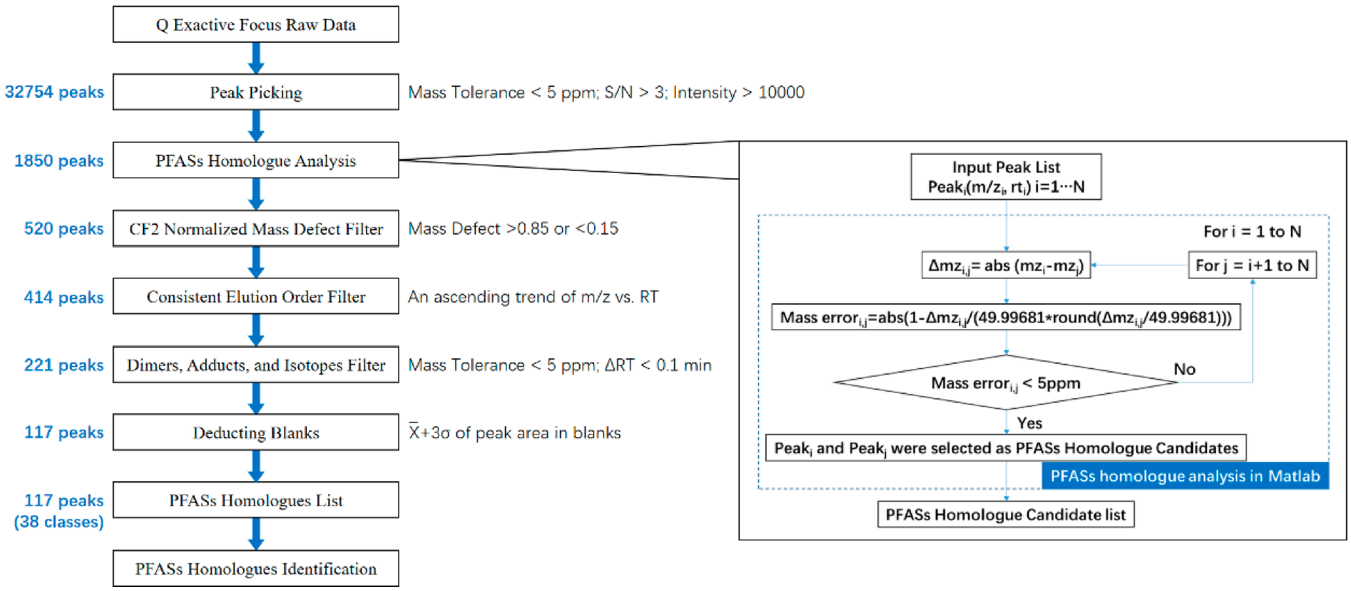

Figure 2. Workflow for nontarget analysis of PFASs and schematic diagram of MATLAB script for PFASs homologue analysis.

(118°57′36.7″ E, 32°7′22.6″ N), from October 2017 to March 2018 using the CAS described previously, and the nearest industrial pollution sources are about 20 km away from the sampling site. The sampling process lasted for 48 h with a flow rate of 20 L min^{-1}. The quartz fiber filters used in the impactor of the NPS were prebaked at 350 °C for 3 h, and the tubes and containers of the CMS were ultrasonicallt cleaned with methanol before sampling. The temperature of the electrical cryo-traps in the cold trap was set to −10 °C.

After sampling had taken place, the filters were folded in aluminum foil and packed into a polyethylene sealed bag. Liquid samples were collected in polypropylene bottles, and the tubes and containers of the CMS were cleaned with 5 mL of methanol, which was collected together with the sample. All samples were stored at 4 °C before extraction and analysis.

Sample Preparation. Preparation methods for quartz fiber filter samples and liquid samples from our previous studies were used for sample preparation (details in Supporting Information section 2).[29,32] Briefly, quartz fiber filters were ultrasonically extracted four times at 40 °C using methanol in polypropylene centrifuge tubes, while liquid samples were enriched by solid-phase extraction with Oasis MAX, Oasis MCX, and Oasis HLB cartridges (6 cc, 500 mg, Waters, Ireland), respectively. Precondition and elution solutions for each cartridge are described in Table S2. All of the extract and eluent were collected in polypropylene centrifuge tubes separately and concentrated to 1 mL by evaporation under nitrogen. Finally, these concentrates were passed through a polypropylene-membrane syringe filter (Acrodisc GHP, 13 mm, 0.2 μm, Waters, U.S.) and stored in polypropylene vials before analysis.

The unused 10% methanol aqueous solution and prebaked filters were extracted using the same preparation method into samples for use as procedural blanks. In addition, all containers and props were precleaned with methanol to avoid contamination.

UPLC−HRMS Analysis. The instrument system consists of an ultraperformance liquid chromatography (UPLC) system (UltiMate 3000 Series, Thermo Fisher Scientific, Bremen, Germany) and a high-resolution orbitrap mass spectrometer (Q Exactive Focus, Thermo Fisher Scientific, Bremen, Germany) with an electrospray ionization (ESI) source. A C18 column (ACQUITY UPLC BEH C18, 1.7 μm, 2.1 × 150 mm, Waters, Ireland) was used for sample separation with 2 mM ammonium acetate 5% methanol in water and methanol as the mobile phase. The Q Exactive Focus was operated in full MS (resolution = 70 000) and discovery mode dd-MS^2 (resolution = 17 500). Detailed instrumental analysis parameters are listed in Supporting Information section 3.

Prior to the sample being analyzed, the instrument was calibrated using a calibration solution (Pierce ESI Calibration Solution, Thermo Fisher Scientific, U.S.) to establish the mass error (<5 ppm) of the instrument. Standards were measured to monitor the fluctuations of the instrument response every five samples during the analysis. To test the sensitivity of the instrument in nontarget analysis, several existing PFAS standards were tested, and all of them were detected at concentrations of 1 and 5 μg/L (Table S4). To test the potential PFASs contamination of the method, the procedural blank was tested, and only PFOA (3.6 pg/m^3), PFPeA (2.5 pg/m^3), and PFOS (1.8 pg/m^3) were detectable.

Nontarget Screening and Identification of PFASs. The integral nontarget analysis flowchart is shown in Figure 2. The peak picking process of the raw data is implemented by Compound Discoverer 3.0 (Thermo Fisher Scientific) using the functions Select Spectrum, Align Retention Time, Detect Compounds, and Group Compounds. PFAS homologue classification used the same method as that described in our previous studies.[32] Briefly, potential PFAS homologues were found by searching the mass difference of 49.99681 Da (CF_2) among peaks using a MATLAB (R2016a) script for PFASs homologue analysis (Figure 2). Mass defects of extracted peaks based on the CF_2 group were calculated according to a previous study,[47] and peaks with mass defects >0.85 or <0.15 were retained. Furthermore, the retention time (RT) should increase as the mass increases for the homologues in each class.[27] Dimers, adducts, and isotopes were checked in extracted peaks with the same RT (RT error < 0.3 min). For the peaks detected in the blank, the mean plus three times the

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Homologue	Serial Number	Formula	Theoretical m/z ([M-H]⁻)	Level
Class 1 PFCAs	A01	C4HF7O2	212.97920	2
	A02	C5HF9O2	262.97601	1
	A03	C6HF11O2	312.97281	1
	A04	C7HF13O2	362.96962	1
	A05	C8HF15O2	412.96643	1
	A06	C9HF17O2	462.96323	1
	A07	C10HF19O2	512.96004	1
	A08	C12HF23O2	612.95365	1
Class 2 PFSAs	B01	C6HF13O3S	398.93660	1
	B02	C8HF17O3S	498.93021	1
Class 3 n:2 FTSs	C01	C8H5F13O3S	426.96791	1
Class 4 Cl-PFESAs	D01	C8HClF16O4S	530.89558	1
Class 5 diPAPs	E01	C16H9F26O4P	788.97505	2
	E02	C18H9F30O4P	888.96866	2
Class 6 H-PFCAs	F01	C7H2F12O2	344.97904	3
	F02	C8H2F14O2	394.97585	3
	F03	C9H2F16O2	444.97265	3
	F04	C10H2F18O2	494.96946	3
	F05	C11H2F20O2	544.96627	3
	F06	C12H2F22O2	594.96307	3
	F07	C13H2F24O2	644.95988	3
	F08	C14H2F26O2	694.95669	3
	F09	C15H2F28O2	744.95349	3
	F10	C16H2F30O2	794.95030	3
	F11	C17H2F32O2	844.94710	3
	F12	C19H2F36O2	944.94072	3
Class 7 *	**G01**	**C7HClF14O3**	**432.93179**	**3**
Cl-PFDEA	**G02**	**C8HClF16O3**	**482.92860**	**3**
	G03	**C9HClF18O3**	**532.92540**	**3**
	G04	**C10HClF20O3**	**582.92221**	**3**
	G05	**C11HClF22O3**	**632.91902**	**3**
Class 8 *	**H01**	**C9HClF18O4**	**548.92032**	**3**
Cl-PFTrEA	**H02**	**C10HClF20O4**	**598.91712**	**3**
	H03	**C11HClF22O4**	**648.91393**	**3**
	H04	**C12HClF24O4**	**698.91074**	**3**
Class 9 *	**I01**	**C11HClF22O5**	**664.90885**	**3**
Cl-PFTeEA	**I02**	**C12HClF24O5**	**714.90565**	**3**
Class 10 *	**J01**	**C12HCl2F21O6**	**708.87421**	**3**
2Cl-PFTeECA	**J02**	**C13HCl2F23O6**	**758.87102**	**3**
Class 11 *	**K01**	**C13H2ClF23O6**	**724.90999**	**4**
H,Cl-PFTeECA	**K02**	**C16H2ClF29O6**	**824.90360**	**4**
Class 12 n:2 FTAs	L01	C5H3F7O2	226.99485	4
	L02	C8H3F13O2	376.98527	4
	L03	C10H3F17O2	476.97888	4
	L04	C12H3F21O2	576.97249	4
Class 13 1:n PFECAs	M01	C4HF7O3	228.97411	4
	M02	C5HF9O3	278.97092	4
	M03	C15HF29O3	778.93898	4

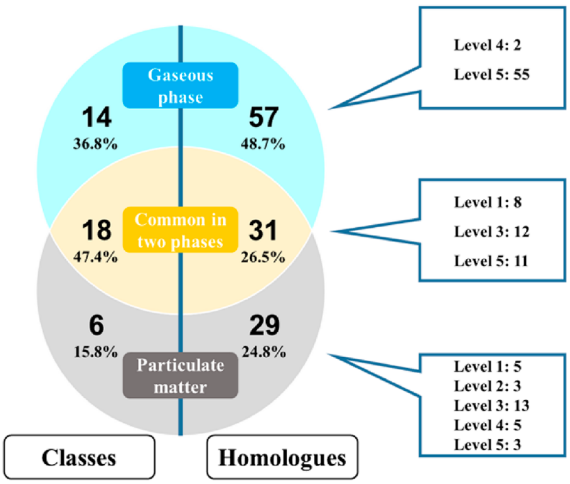

Figure 3. PFAS homologues identified as Level 4 or above and quantity distribution of PFAS homologue classes and homologues in atmosphere with the identification confidence noted. *Classes in bold font are the PFAS homologues that are reported for the first time in this study.

standard deviation of the peak area in the three blanks was deducted.

To identify the potential PFASs homologues, the accurate m/z value of the extracted peaks was screened in the database. The database includes the laboratory's existing standards (Table S1), the PFASs we have identified in previous studies,[29,32] and the PFASs with MS/MS spectrum information in the Norman database.[48] For homologues with m/z matching to the database, MS/MS spectra were compared to the database to confirm their structures. For other homologues, Compound Discoverer 3.0 (function Predict Compositions) and Qual Browser (Thermo Fisher Scientific) were used to calculate the formulas of molecules and fragments in the MS/MS spectrum (molecular mass tolerance 5 ppm and fragments mass tolerance 5 mDa). SIRIUS and CSI:FingerID were also used to assist in the determination of molecular formulas and structures.[49] On the basis of the criteria established in previous study,[50] we have assigned confidence levels (Levels 1−5) for the discovered PFASs. For Level 1, the structure was identified by standards. For Level 2, the structure was identified by library spectrum (Level 2a) or diagnostic evidence (Level 2b). For Level 3, the substructure was identified by the MS/MS spectra, while the connection of substructure was uncertain and isomers existed. For Level 4, the unique molecular formula was retained after considering limiting factors such as the number of elements and degree of unsaturation for PFASs. For Level 5, the peaks were retained after the PFAS homologue analysis. Details of nontarget screening and identification are shown in Supporting Information section 4.

Data Analysis. Microsoft Office Excel 2010 was used for data analysis to deduct procedural blanks and analyze the distribution of PFAS in different components of air.

RESULTS AND DISCUSSION

Discovery of PFAS Homologues in the Atmosphere. According to the method of PFAS homologues nontarget analysis described above, 1850 peaks were found by first detecting the mass difference of 49.99681 Da (CF_2). 221 peaks were retained after filtering on the basis of mass defect and retention time as well as removing dimers, adducts, and isotopes. Finally, 38 classes (117 homologues) were selected as potential PFAS homologues after subtracting the blank (Figure 2). Among them, 13 classes (48 homologues) were identified as Level 4 or above as listed in Figure 3 (details are provided in Table S5), and other potential PFAS homologues are listed in Table S7 as Level 5.

Class 1. Eight PFCA homologues were identified in this class, with C5−10 and C12 PFCAs all confirmed at Level 1 by the standard. The mass error of the eight PFCA homologues among all samples ranged from 0.01−2.53 ppm, and the retention time gaps as compared to the standard were less than 0.27 min. Detailed comparison of the MS/MS spectrum with the standard is shown in Figure S1.

Class 2. PFOS and perfluorohexanesulfonate (PFHxS) were confirmed at Level 1 by the standard as PFSAs. A mass error of 0.09−2.39 ppm was noted, while the RT tolerance ranged from 0.08−0.20 min. The MS/MS spectrum of PFOS in the sample as compared to the standard is provided in Figure S2.

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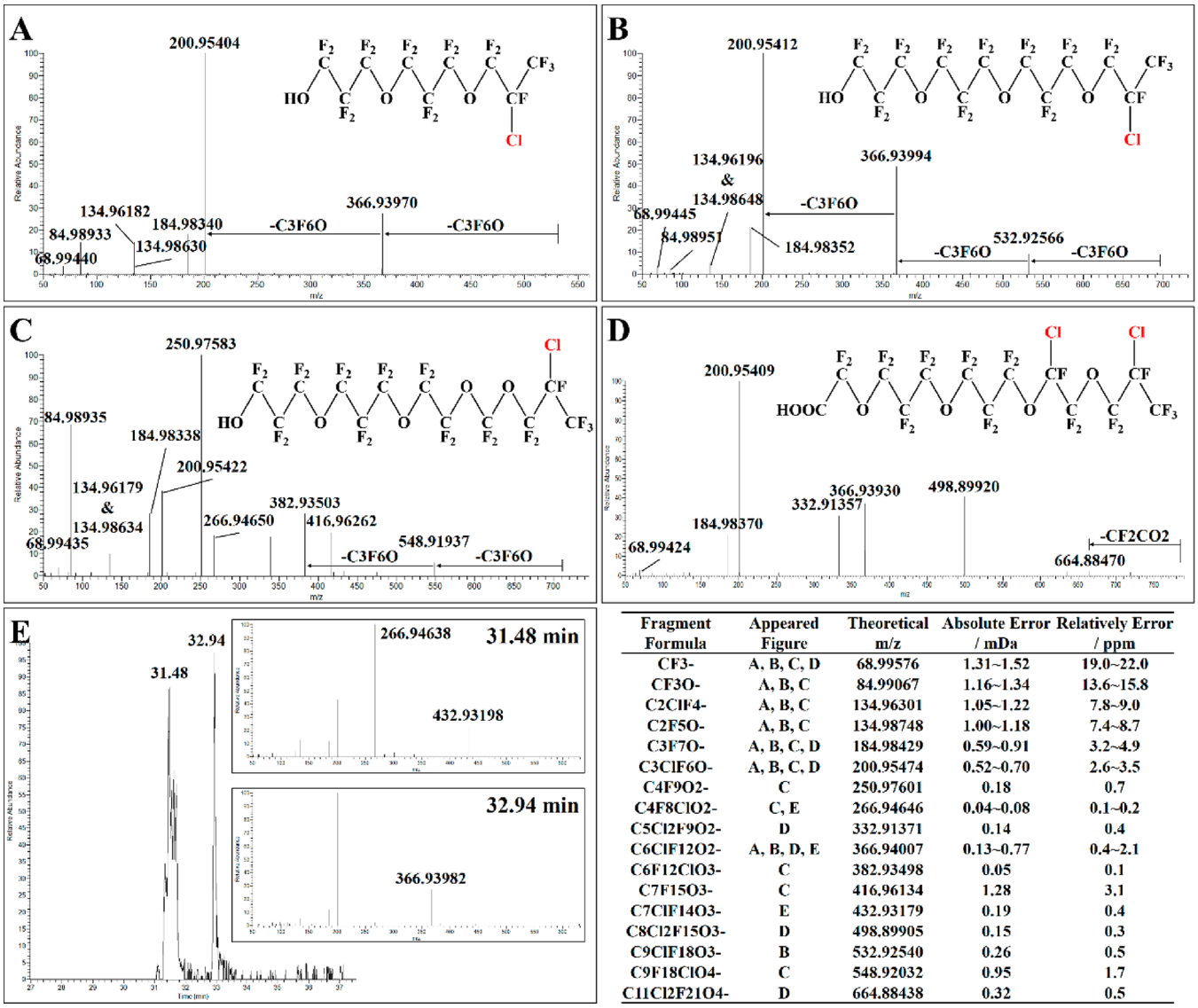

Fragment Formula	Appeared Figure	Theoretical m/z	Absolute Error / mDa	Relatively Error / ppm
CF3-	A, B, C, D	68.99576	1.31~1.52	19.0~22.0
CF3O-	A, B, C	84.99067	1.16~1.34	13.6~15.8
C2ClF4-	A, B, C	134.96301	1.05~1.22	7.8~9.0
C2F5O-	A, B, C	134.98748	1.00~1.18	7.4~8.7
C3F7O-	A, B, C, D	184.98429	0.59~0.91	3.2~4.9
C3ClF6O-	A, B, C, D	200.95474	0.52~0.70	2.6~3.5
C4F9O2-	C	250.97601	0.18	0.7
C4F8ClO2-	C, E	266.94646	0.04~0.08	0.1~0.2
C5Cl2F9O2-	D	332.91371	0.14	0.4
C6ClF12O2-	A, B, D, E	366.94007	0.13~0.77	0.4~2.1
C6F12ClO3-	C	382.93498	0.05	0.1
C7F15O3-	C	416.96134	1.28	3.1
C7ClF14O3-	E	432.93179	0.19	0.4
C8Cl2F15O3-	D	498.89905	0.15	0.3
C9ClF18O3-	B	532.92540	0.26	0.5
C9F18ClO4-	C	548.92032	0.95	1.7
C11Cl2F21O4-	D	664.88438	0.32	0.5

Figure 4. Identification of chlorinated polyether PFASs. (A) MS/MS spectrum and proposed structure of G03 in Class 7. (B) MS/MS spectrum and proposed structure of H04 in Class 8. (C) MS/MS spectrum and proposed structure of I02 in Class 9. (D) MS/MS spectrum and proposed structure of J02 in Class 10. (E) Extract ion chromatogram and MS/MS spectrum of two isomers in Class 8. The fragment information in the above MS/MS spectrum is listed in the table. The red part of the structure indicates the uncertain substituent.

Class 3. Only one homologue was detected in this class after subtracting the blank, which was identified as 6:2 fluorinated telomer sulfonate (6:2 FTS) and confirmed at Level 1 by the standard. The mass error of 6:2 FTS in different samples ranged from 0.05−1.35 ppm. As compared to the standard, the RT tolerance ranged from 0.06−0.22 min, and five fragments all matched with the mass error from −1.56 to 1.52 mDa (Figure S3). 6:2 FTS has been detected in airborne particulate matter[32] and surface water[51] in China in previous studies, and it was considered a novel alternative to PFOS[52] and a degradation product of fluorosurfactants.[53,54]

Class 4. This class was identified as chlorinated polyfluorinated ether sulfonate (Cl-PFESA) through database screening with a mass error of 0.08−1.29 ppm. As for the MS/MS spectrum comparison, only the most abundant fragment $C_6F_{12}ClO^-$ (350.94043, 4.8 mDa) of 6:2 Cl-PFESA in the database was observed in the sample due to the low content of the parent species in the sample. For further confirmation, a standard of 6:2 Cl-PFESA was measured, and the peak in the sample was confirmed with a mass error of 0.57 ppm and a RT tolerance of 0.13 min (Figure S4). Thus, this peak was identified as 6:2 Cl-PFESA with Level 1. The commercial name of Cl-PFESA is F-53B, which has been widely used as a substitute for PFOS in China for more than 30 years.[55] 6:2 Cl-PFESA has already been detected in surface water,[51] fish,[13] airborne particulate matter,[32] and human serum and placenta[14] and has stronger bioaccumulation and biotoxicity than does PFOS.[13−17]

Class 5. Two polyfluoroalkyl phosphoric acid diesters (diPAPs), 6:2 diPAP and 6:2,8:2 diPAP, were identified by database screening as Level 2a with a mass error of 0.44−4.35 ppm. The MS/MS spectrum is shown in Figure S5. This class of PFASs has been previously reported in airborne particulate matter.[32]

Class 6. In this class, the molecular formula of 10 PFAS homologues was determined as $C_nF_{2n-2}O_2H_2$ with a mass error of 0.09−3.20 ppm. This class was identified as hydro-substituted PFCAs (H-PFCAs) because the MS/MS spectrum

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of the homologues all have $[M - 64]^-$ fragments, which correspond to the neutral loss of CO_2 and HF, as well as a series of fragments corresponding to the mass of the fluorocarbon chain such as $C_nF_{2n+1}^-$ (118.99265 of $C_2F_5^-$, 168.98937 of $C_3F_7^-$, and 218.98618 of $C_4F_9^-$) and $C_nF_{2n-1}^-$ (280.98298 of $C_6F_{11}^-$ and 330.97979 of $C_7F_{13}^-$). Some of the above three feature fragments were observed in the C7 H-PFCA standard and the previous study of H-PFCAs[26] (Figure S6), but the homologues detected in this study cannot be confirmed as Level 1 due to that the position of hydrogen substitution on the fluorocarbon chain cannot be confirmed by the MS/MS spectrum. Therefore, they can only be confirmed as Level 3. Although H-PFCAs have already been detected in wastewater[29] and surface water,[56] this is the first time that H-PFCAs have been detected in air samples.

Class 7. According to the 3:1 isotope distribution of the isotope peaks $[M]^-$ and $[M + 2]^-$ (Figure S7), the molecules of this class contain a chlorine atom. The molecular formula of the five homologues is inferred as $C_nHClF_{2n}O_3$ with a mass error of 0−2.35 ppm in all samples. We observed fragments m/z 68.99440 (CF_3^-, 1.36 mDa), 84.98933 (CF_3O^-, 1.34 mDa), 134.98630 ($C_2F_5O^-$, 1.18 mDa), and 184.98340 ($C_3F_7O^-$, 0.89 mDa) in the MS/MS spectrum of G03 ($C_9HClF_{18}O_3$, refer to the table in Figure 3) shown in Figure 4A, which are the same as in the MS/MS spectrum of perfluoroalkyl alcohol.[29] Therefore, one end of the carbon chain should be an alcoholic hydroxyl group. Three chlorine-containing fragments m/z 134.96182 ($C_2ClF_4^-$, 1.19 mDa), 200.95404 ($C_3ClF_6O^-$, 0.70 mDa), and 366.93970 ($C_6ClF_{12}O_2^-$, 0.37 mDa) were also observed in the MS/MS spectrum of G03 together with the neutral losses of C_3F_6O and $C_6F_{12}O_2$ (Figure 4A), which indicated that the molecule is linear with two ether bonds separated by three carbons with a chlorine-containing group on the other end. G02 ($C_8HClF_{16}O_3$, refer to the table in Figure 3) did not have the fragment $C_3F_7O^-$ and only had the neutral loss of $C_5F_{10}O_2$; thus the position of the ether bond was uncertain in the carbon chain. For G01 ($C_7HClF_{14}O_3$, refer to the table in Figure 3), we found three chromatographic peaks with different retention times (28.31, 30.51, and 32.21 min) at this mass (Figure S8). The 28.31 min substance should be a homologue of this class due to the growth trend of m/z and RT, and the others may be isomers. Overall, this class was identified as chlorinated perfluorodiether alcohols (Cl-PFDEAs). We consider that the chlorine atom is not in the terminal position but rather on the second carbon atom, because only $C_2ClF_4^-$ is observed without $CClF_2^-$. However, there was not enough evidence to confirm the position of the chlorine atom, and as such Class 7 can only be confirmed as Level 3. Generally, fluorotelomer alcohol had little to no response in ESI^- as an $[M - H]^-$ peak and was only seen as an acetate adduct. When the position of the OH group was located at the perfluorinated carbon atom, the acidity will be stronger, because the strongly electronegative fluorines withdraw electrons from the carbon and inductively stabilize the anion on oxygen atom. Therefore, the perfluoroalcohols have a stronger acidity than do the fluorotelomer alcohols. The predicted pK_a of perfluoroalcohols is about 3−4 by the online tool in ChemAxon (https://chemaxon.com/), which supported the negative ionization mode, while the predicted pK_a of fluorotelomer alcohols is about 14−15. To the best of our knowledge, this is the first report of chlorinated perfluoropolyether alcohols, denoting the discovery of a new class of PFASs.

Class 8. The molecular weights of this class were 16 Da greater than those of Class 7, and the general molecular formula of the four homologues was identified as $C_nHClF_{2n}O_4$ with a mass error of 0.02−2.07 ppm, which has one more oxygen atom than Class 7. Neutral losses of C_3F_6O, $C_6F_{12}O_2$, and $C_9F_{18}O_3$ were observed in the MS/MS spectrum of H04 ($C_{12}HClF_{24}O_4$, refer to the table in Figure 3), and the fragments CF_3^-, CF_3O^-, $C_2F_5O^-$, $C_3F_7O^-$, $C_2ClF_4^-$, and $C_3ClF_6O^-$ were also observed similar to the case of Class 7 with mass errors of 0.13−1.31 mDa (Figure 4B). This indicates that H04 has the same terminal substituent as Class 7, but has three ether bonds separated by three carbons. Therefore, this class was identified as chlorinated perfluorotriether alcohols (Cl-PFTrEAs) at Level 3 due to the uncertainty of the chlorine substitution position. The only difference between H04 and H03 ($C_{11}HClF_{22}O_4$, refer to the table in Figure 3) was that the largest ion fragment changed from $C_9ClF_{18}O_3^-$ to $C_8ClF_{16}O_3^-$ (m/z 482.92643, 1.6 mDa), which showed that the loss of CF_2 occurred between the first and the second ether bonds from the hydroxyl group. However, H02 ($C_{10}HClF_{20}O_4$, refer to the table in Figure 3) has two different chromatographic peaks that differ by 1.5 min, and the fragments in MS/MS spectrum change from 366.93982 ($C_6ClF_{12}O_2^-$, 0.25 mDa) to 266.94638 ($C_4ClF_8O_2^-$, 0.08 mDa) and 432.93198 ($C_7ClF_{14}O_3^-$, 0.19 mDa) (Figure 4E). This indicates that H02 has two isomers with different ether bond positions. It is the first time that this class has been discovered. The carbon chain of this class (C9−12) is longer than that of Class 7 (C7−11), which may be due to an increase in the number of ether bonds.

Class 9. Two homologues of this class were identified as chlorinated perfluorotetraether alcohols (Cl-PFTeEAs, $C_nHClF_{2n}O_5$) at Level 3, having one more oxygen atom than Class 8 and a mass error of 0.15−2.63 ppm. The fragments CF_3^-, CF_3O^-, $C_2F_5O^-$, $C_3F_7O^-$, $C_2ClF_4^-$, and $C_3ClF_6O^-$ shown in the MS/MS spectrum of I02 ($C_{12}HClF_{24}O_5$, refer to the table in Figure 3) indicated that the structure at both ends is the same as that in Classes 7 and 8 (Figure 4C). The neutral loss of C_3F_6O suggests that there is an ether bond between the third and fourth carbons at the beginning of the hydroxyl group, and the neutral loss of $C_6F_{12}O_2$ means there is another ether bond between the sixth and seventh carbons. In addition, we also speculate that the other two ether bonds exist on both sides of the ninth carbon due to the fragments m/z 266.94650 ($C_4F_8ClO_2^-$, 0.04 mDa) and 200.95422 ($C_3ClF_6O^-$, 0.52 mDa). For I01 ($C_{11}HClF_{22}O_5$), we cannot accurately speculate on the location of its ether bond because only two long-chain fragments m/z 266.94604 ($C_4F_8ClO_2^-$, 0.42 mDa) and 366.93948 ($C_6F_{12}ClO_2^-$, 0.59 mDa) were observed. The smallest homologue we found in this class was C11 chlorinated perfluorotetraether alcohol, where the carbon chain length of chlorinated perfluoropolyether alcohol increases with the number of ether bonds as compared to Classes 7 and 8. Chlorinated perfluoropolyether alcohols (Classes 7−9) were a substructure of chlorinated perfluoropolyether carboxylic acids (a complex process mixture, C_3F_6ClO-$[CF_2CF(CF_3)O]_n$-$[CF(CF_3)O]_m$-CF_2COOH, has been registered at the European Food Safety Authority,[57] CAS no. 329238-24-6), which were produced by Solvay and used as PFOA alternatives for fluoropolymer manufacture.[58] The substructure of the copolymer of perfluoro-1,2-propylene glycol and perfluoro-1,1-ethylene glycol could support the neutral loss of C_3F_6O and C_2F_4O and the fragments of $C_2F_5O^-$

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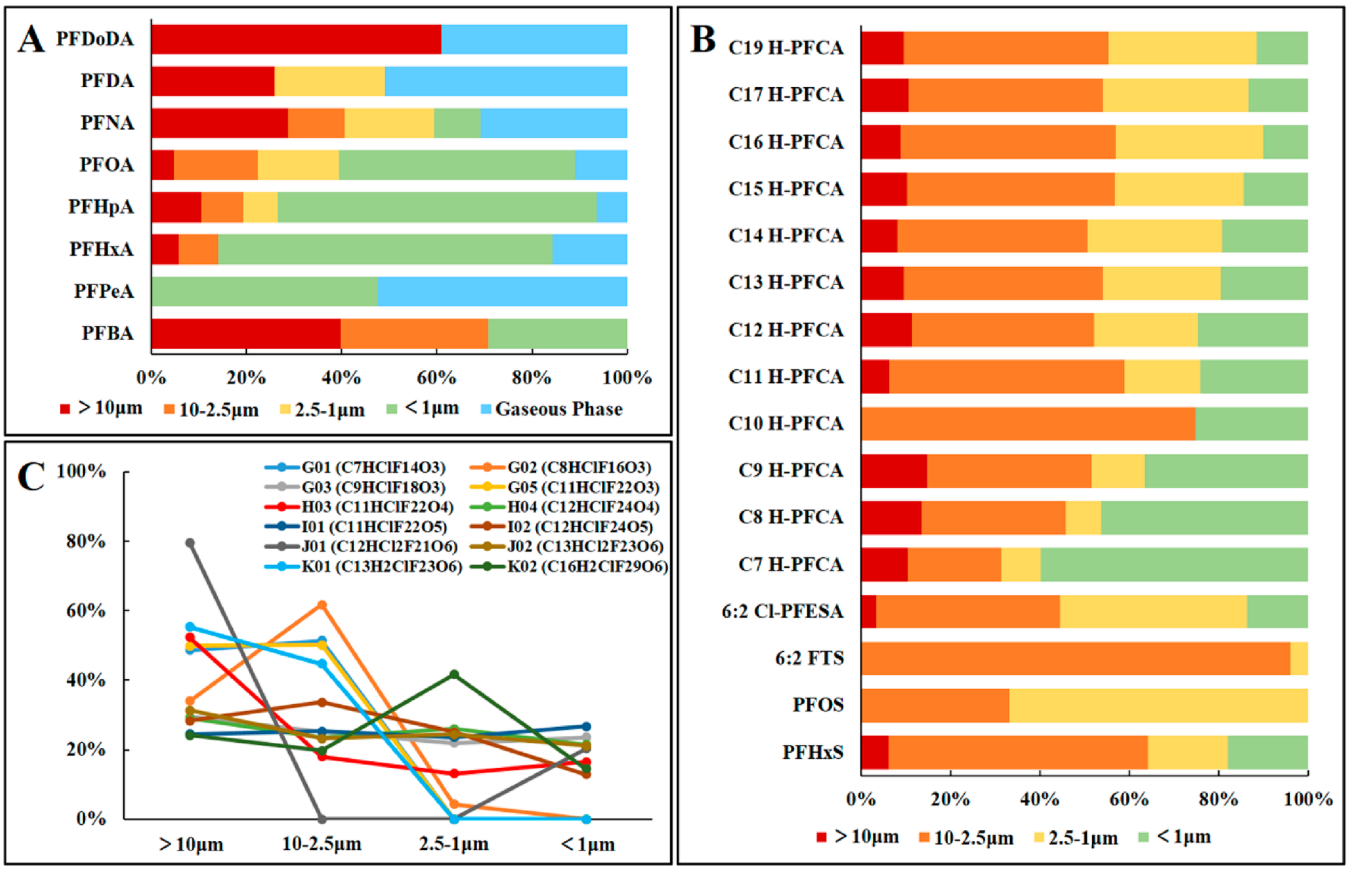

Figure 5. Phase distribution and particle size distribution of PFAS homologues. (A) Distribution of 8 PFCAs in Class 1. (B) Particle size distribution of 2 PFSAs in Class 2, 6:2 FTS in Class 3, 6:2 Cl-PFESA in Class 4, and 12 H-PFCAs in Class 6. (C) Particle size distribution of homologues in Classes 7−10.

and $C_3F_7O^-$ in the MS/MS spectra. Considering structural similarity with GenX, we speculated that chlorinated perfluoropolyether alcohols could be the transformation products of chlorinated perfluoropolyether carboxylic acids by the removal of a perfluoroacetic acid group.[59]

Classes 10 and 11. Class 10 was identified as dichlorinated perfluorotetraether carboxylic acids (2Cl-PFTeECAs), which can be expressed using the molecular formula $C_nHCl_2F_{2n-3}O_6$ with a mass error of 0.25−1.28 ppm based on the exact mass and the isotopic distribution in Figure S11. The MS/MS spectrum of J02 ($C_{13}HCl_2F_{23}O_6$, refer to the table in Figure 3) is given in Figure 4D. The mass loss of 93.98632 ($CF_2CO_2^-$, 0.86 mDa) in J02 indicated that the molecule contains a carboxyl group, and the ion fragments m/z 664.88470 ($C_{11}Cl_2F_{21}O_4^-$, 0.32 mDa), 498.89920 ($C_8Cl_2F_{15}O_3^-$, 0.15 mDa), 366.93930 ($C_6ClF_{12}O_2^-$, 0.77 mDa), 332.91357 ($C_5Cl_2F_9O_2^-$, 0.14 mDa), 200.95409 ($C_3ClF_6O^-$, 0.65 mDa), and 184.98370 ($C_3F_7O^-$, 0.59 mDa) revealed its perfluoropolyether structures with two chlorine-substituted, which can be identified at Level 3 due to possible variation in the substitution position. For Class 11, the molecular formula of the two homologues can be expressed as $C_nH_2ClF_{2n-3}O_6$ with a mass error of 0.11−1.28 ppm based on the isotopic distribution in Figure S12. The structures of this class cannot be accurately identified due to the lack of MS/MS spectrum, but because their molecular formula is very similar to that of Class 10 (only one chlorine atom is replaced by a hydrogen atom) and the retention time is close, we considered that they are hydrosubstituted chlorinated perfluorotetraether carboxylic acids (H,Cl-PFTeECAs) at Level 4. It has been reported that hydrosubstituted polyfluorinated ether sulfonate was the transformation product of Cl-PFESAs.[30] Thus, we speculated that H,Cl-PFTeECAs could be the transformation product of 2Cl-PFTeECAs. Chlorinated perfluoropolyether carboxylic acids (C_3F_6ClO-$[CF_2CF(CF_3)O]_n$-$[CF(CF_3)O]_m$-CF_2COOH, CAS no. 329238-24-6) from Solvay were used as PFOA alternatives for fluoropolymer manufacture,[58] which have been first detected in the Bormida river. In this study, we also detected chlorinated perfluoropolyether carboxylic acids, which contain two chlorine atoms or one hydrogen atom plus one chlorine atom. Therefore, dichlorinated perfluoropolyether carboxylic acids and hydrosubstituted chlorinated perfluoropolyether carboxylic acids are the first discoveries in the environment.

Class 12. This class was identified as n:2 fluorinated telomer acids (FTAs) through database screening with mass error < 4.15 ppm. We confirmed two of the homologues ($C_{10}H_3F_{17}O_2$, 8:2 FTA and $C_{12}H_3F_{21}O_2$, 10:2 FTA) using standards with an RT tolerance of 0.16−0.34 min. The other two homologues can only be judged as Level 4 due to the poor MS/MS spectrum information because abundance in the sample was too low. This class has been previously detected in airborne particulate matter.[32] Similar to n:2 FTSs, they are also used as a substitute for traditional PFASs.[52]

Class 13. The molecular formula of the three homologues in this class can be expressed as $C_nHF_{2n-1}O_3$ with a mass error of 0.10−4.89 ppm. We speculate that this class is 1:n polyfluoroalkyl ether carboxylic acids (PFECAs) through

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database screening, but it can only be confirmed at Level 4 because of the poorly resolved MS/MS spectrum with excessive impurity fragments. 1:n PFECAs have been discovered in surface water[27] and airborne particulate matter.[32] PFECAs can be used as a substitute for PFCAs, and previous studies have shown that some PFECAs, such as HFPO-TA, have stronger bioaccumulation and biotoxicity as compared to PFOA.[18−20]

Other Potential PFAS Homologues. In addition to the above 13 classes of PFAS homologues identified as Level 4 or above, there are 25 classes of potential PFASs homologues found as Level 5, which are listed in Table S7 without molecular formulas. Their structures are difficult to determine due to the uncommon ion fragments or lack of MS/MS spectrum information.

Distribution of PFASs in the Gaseous Phase and Particulate Matter. The above-mentioned 38 classes and 117 homologues of PFASs discovered by nontarget analysis were distributed in the atmosphere particulate matter and gaseous phase, as shown in Figure 3. The classes and homologues that were only present in the particulate matter account for 15.8% and 24.8% of the total, respectively, while a large number of potential novel PFASs were found in the gaseous phase. As far as we know, this study is the first nontarget analysis of unknown PFASs in the atmospheric gaseous phase.

Eight of the classes described above have been previously reported: PFCAs, PFSAs, n:2 FTSs, Cl-PFESAs, diPAPs, H-PFCAs, n:2 FTAs, and 1:n PFECAs. Among these, H-PFCAs were first discovered in the atmosphere, while n:2 FTSs, n:2 FTAs, and 1:n PFECAs have only been reported in previous nontarget studies without atmospheric distribution.[32]

Most of the PFCAs were detected in both the gaseous phase and the particular matter (Figure 5A). PFBA was detected only in the particular matter. For the particle size distribution, PFPeA, PFHxA, PFHpA, and PFOA were mainly distributed in the <1 μm particular matter, while the other PFCAs preferred to absorb to the >10 μm particular matter. The difference in distribution may reveal different sources among PFCAs homologues.

PFSAs were only detected in the particulate matter. Unlike PFOA, PFHxS and PFOS were aggregated in coarse particles of 10−2.5 μm and 2.5−1 μm in size instead of in finer particles, respectively (Figure 5B). This phenomenon has also been reported in several previous studies, showing significant differences from PFCAs.[40,60,61] Similar distributions were observed in n:2 FTSs, H-PFCAs, and Cl-PFESAs (Figure 5B). We only observed 6:2 FTS in the two particle fractions of the particulate matter, and the 10−2.5 μm particle fraction contains approximately 96% of the total. Six of the twelve observed H-PFCAs homologues were detected in the gaseous phase, and the fraction of these H-PFCAs in the gaseous phase was below 4% (Table S5), a marked difference from PFCAs; it was indicated that H-PFCAs could be the degradation product of PFCAs in particle matter. For H-PFCAs with more than 8 carbon atoms, the 10−2.5 μm particle fraction is the most easily distributed, revealing rules similar to those for the PFCAs in the study by Harada et al.[62] The <1 μm particle fraction is the most easily distributed for H-PFCAs with 7 or 8 carbon atoms (Table S5). For 6:2 Cl-PFESA, the 10−2.5 μm and 2.5−1 μm particle fractions accounted for 83% of the total intensity. However, due to that the gaseous PFASs may be adsorbed on quartz fiber filters during the particulate matter collection, the fraction of gaseous PFASs in these classes may be underestimated.

As for diPAPs, n:2 FTAs, and 1:n PFECAs, because the homologues in these classes were only detected in a single component, their distributions could not be discussed. Details of the detection of these classes are given in Table S5.

Five classes of chlorinated perfluoropolyether substances were discovered for the first time in this study. This kind of novel PFAS is mainly distributed in airborne particulate matter. A more obvious phenomenon of the three classes of chlorinated perfluoropolyether alcohols was detected together in the particulate matter and gaseous phase, while two classes of chlorinated perfluoropolyether carboxylic acid were found in particulate matter (Table S5). Previous study indicates that PFASs can be divided into ionizable PFASs (ex. perfluoroalkyl acids) and neutral PFASs (ex. FTOHs and FOSAs); ionizable PFASs have stronger affinity with particulate matter, and neutral PFASs are more likely to be distributed in the gaseous phase,[36] a pattern that is followed by our results. Furthermore, in the particle size distribution of the particulate matter, we found that most detected substances tend to be distributed over coarse particle fractions (Figure 5C). Some similar substances such as Cl-PFESA have been reported in the atmosphere, but only in the particulate matter without examination of the particle size distribution,[32,63] and previous studies has discovered perfluorinated ether acids in surface waters in North America by nontarget screening,[64] denoting the global occurrence of novel perfluoropolyether substances as substitutes for traditional compounds or their environmental degradation products. Cl-PFESAs (considered as a substitute for PFOS) and hexafluoropropylene oxide trimer acid (HFPO-TA, considered as a substitute for PFOA) with chemical structures similar to those in our findings have been confirmed to have greater biotoxicity and bioaccumulation as compared to their predecessors,[13−20] which suggest that chlorinated or ether-containing modifications may increase the biological toxicity of PFASs and cause more serious environmental risks. Therefore, these chlorinated perfluoropolyether substances should be further quantified and considered in the risk assessments of PFASs.

In addition to the above classes, we also found 25 other classes of potential PFAS homologues at Level 5, while 14 classes were only detected in the gaseous phase (Table S7). Given that they have positive mass defects unlike most known PFASs and the acquired fragments of the MS/MS spectrum are uncommon, we cannot make an accurate identification of their structures. However, some patterns can still be observed. Most of these have lower molecular weights (<400 Da), which makes sense as short-chain PFASs are more easily distributed in the gaseous phase. In addition, we consider that the fluorine content of these substances will be less than that of traditional PFASs due to their positive mass defects of molecules and fragments. Chen and co-workers have already discovered that there are a large number of unknown short-chain PFASs from the atmosphere present in precipitation from mainland China and have indicated their chemical structures and relevant environmental risks should be of concern,[65] as evidenced by the large number of potential PFASs found at Level 5 in the gaseous phase in this study (Figure 3).

■ IMPLICATIONS AND LIMITATIONS

We used a new type of sampler to simultaneously collect atmospheric particulate matter and gaseous phase samples,

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which can more accurately retain the distribution of PFASs in the atmosphere. We further identified multiple classes of novel PFASs by nontarget analysis. Five classes of chlorinated perfluoropolyether substances were first reported in this study. In reference to previous studies, chlorinated and ether bonded substances may have greater environmental health risks as compared to legacy PFASs, and further research on their toxicity and risk assessment is necessary.

Considering a limited sampling volume, the uncertainty on the recovery of novel PFASs, and data acquired by UPLC–HRMS in negative mode in this study, there are still several emerging or unknown PFASs not discovered, and we may underestimate the contribution of PFASs in the gaseous phase. In future studies, more mass spectrometry information needs to be collected and more effective structural identification methods must be used to identify potential short-chain PFASs in the gaseous phase, which may contain a large number of unknown novel PFASs. Nontargeted analytical methods based on high-resolution gas chromatography–mass spectrometry should be considered in future studies due to the large amount of nonpolar substances in the atmosphere.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b05457.

> Standards and reagents, sample preparation, UPLC–HRMS analysis, nontarget screening and identification of PFASs, structure elucidation of peaks, the MS/MS spectrum of the peaks, Tables S1–S7, and Figures S1–S12 (PDF)

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Notes

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