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# Quantification of perfluorinated compounds in atmospheric particulate shows potential connection with environmental event

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## ABSTRACT

A method of quantification of perfluorinated compounds (PFCs) from atmospheric particulate matter (APM) is described. A single step pretreatment method, selective pressurized liquid extraction (SPL), was developed to reduce the high matrix background and avoid contamination from commonly used multiple sample pretreatment steps. An effective sorbent was selected to purify the PFCs during SPL, followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS), for quantification of PFCs. Conditions affecting the SPL efficiency, including temperature, static extraction time, and number of extraction cycles used, were studied. The optimum conditions were found to be 120°C, 10 min, and 3 cycles, respectively. LC-MS/MS method was developed to obtain the optimal sensitivity specific to PFCs. The method detection limits (MDLs) were 0.006 to 0.48 ng/g for the PFCs studied and the linear response range was from 0.1 to 100 ng/g. To ensure accurate values were obtained, each step of the experiment was evaluated and controlled to prevent contamination. The optimized method was tested by performing spiking experiments in natural particulate matter matrices and good rates of recovery and reproducibility were obtained for all target compounds. Finally, the method was successfully used to measure 16 PFCs in the APM samples collected in Beijing over five years from 2015 to 2019. It is observed that some PFCs follow the trend of total PFC changes, and can be attributed to the environment influencing events and policy enforcement, while others don't seem to change as much with time of the year or from year to year.

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## Introduction

Perfluorinated compounds (PFCs) are a class of fluorinated organic molecules that have a particular structure of hydrophobic fluorinated alkyl chain and a polar terminal group (Corsini et al., 2012; Jeong et al., 2019). The special structure of PFCs gives them unique characteristics of both hydrophobicity and lipophobicity (Lancer et al., 2010). They have been used in substances such as surfactants, lubricants, upholstery, polishes, fire-fighting foams, and food packaging (Liu et al., 2020; Ahrens et al., 2012; Calafat et al., 2016), making them omnipresent in the environment (Yamashita et al., 2004). Numerous studies indicate that PFC exposure may induce peroxisome proliferation, immune system disorders, chronic kidney disease, tumorigenesis, hepatotoxicity, liver tumor, pediatric atopy, and behavioral disorders (Bloom et al., 2010; Gump et al., 2011; Wang et al., 2011; Fagbayigbo et al., 2018).

Historically, PFCs were produced and used in longer-chain forms, especially the C6, C8, and C10 types (Paul et al., 2009). However, the persistent, bio-accumulative and toxic properties of long-chain perfluoroalkyl acids (PFAAs) have led to their phasing-out in production by major manufacturers since 2000 (Groffen et al., 2019). In May 2009, perfluorooctane sulfonate (PFOS) and its related substances were listed in Annex B of the Stockholm Convention on Persistent Organic Pollutants, putting global restrictions on their use (Wang et al., 2020). As a result, alternative PFCs, such as C4 to C6 shorter-chain analogues were developed (Wang et al., 2016; Tian et al., 2018; Wang et al., 2011). Although they are less persistent in the biota than the longer chain PFCs, they are also of concern for their persistence in the environment and can potentially cause similar toxic effect as the long chain PFCs. Due to their mass production and usage, PFCs have been consistently detected in the environment, including the atmosphere, water, and soil.

As a class of air pollutants, PFCs' presence in atmospheric particulate matter (APM) have attracted much attention in recent years (Zhang et al., 2016; Ahrens et al., 2011; Shoeib, Harner and Vlahos, 2006). However, the concentrations of PFCs in APM is at trace or ultra-trace level, and the composition of APM is complex, especially in winter haze that contains moisture, inorganic, organic and other polluting chemicals. Such complexity made it difficult to analyze the trace amount of PFCs in APM. An important issue that cannot be ignored is that PFCs exist in the laboratory environment, including containers, reagents, and instrument due to their hydrophobicity, lipophobicity, volatility, and persistence. The existing contaminants makes it difficult to achieve accurate results and good reproducibility when measuring the ultra-trace amount of PFCs in APM. Therefore, contamination control of the entire experimental process is necessary for developing an effective and accurate analytical method. In addition, reducing the steps involved in the analytical process from sample preparation to detection is critically important.

Organic pollutants can be extracted from particulate matter by different extraction techniques such as Soxhlet extraction (SE) (Lu et al., 2018; Krafft and Riess, 2015; Dreyer et al., 2009), ultrasonic-assisted extraction (UAE) (Shoeib et al., 2010;

Song et al., 2016), and pressurized liquid extraction (PLE) (Cai et al., 2012). PLE, also known as accelerated solvent extraction (ASE), has been widely used since US Environmental Protection Agency (US EPA) published the PLE method for the organic extraction from solid samples (Vazquez-Roig and Picó, 2015). PLE can be automated to achieve good repeatability at elevated temperature and pressure (Kim et al., 2019). However, like other solvent-based extraction techniques, target analytes and some non-target analytes (including those that may interfere with quantification) are often co-extracted from the sample matrix. This means that the cleanup process, such as solid phase extraction (SPE) or gel-permeation chromatography (GPC), is often needed to further remove the interfering compounds (Subedi et al., 2015). Due to the complexity of the procedures used, it is often inevitable to introduce more background brought on by the environment and reagents in the detection process, especially for the analysis of trace and ultra-trace amount of PFCs in environmental samples. In order to improve analytical throughput, reduce the loss of analytes and avoid contamination, a simple, easy-to-operate and sensitive method for PFCs is urgently needed (Beck et al., 2008). In recent years, selective PLE (SPLE) was developed by incorporating cleanup-adsorbents within the extraction cell, to extract target analytes and remove potential interfering matrix compounds concurrently (Liu et al., 2009). SPLE has been successfully applied to the analysis of many persistent organic pollutants in airborne particulate matter, soil, and biological samples (Zhang et al., 2017, 2011). However, it has not been used for the analysis of PFCs.

Analytical techniques used for the analysis of APM include gas chromatography with electron-capture detection (GC-ECD), GC-mass spectrometry (GC-MS), and high performance liquid chromatography (HPLC). Liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) in the negative-ion mode with multiple reaction monitoring (MRM) has shown potential to be used for quantifying PFCs in the air at the level of  $\text{pg}\cdot\text{m}^{-3}$  (Li et al., 2018; Lashgari and Lee et al., 2014; Llorca et al., 2009; Noelia et al., 2010), and the repeatability was within 8% with no need for derivatization (Wyndham et al., 2003; Tian et al., 2018).

In this work, an optimized SPLE sample preparation method is developed for both extraction and cleanup of PFCs. In addition, based on the stringent control of each step in the process to prevent sample pollution, a simple, practical and sensitive method for the determination of PFCs in the APM with LC-MS/MS was developed. SPLE can treat the sample in a closed one step process quickly to avoid pollution. The described method significantly reduced the sample preparation time, and efficiently separated, identified, and quantified 16 PFCs. Four factors (absorbent type, absorbent amount, temperature, and cycle number) of SPLE conditions were studied to obtain the optimal extraction/cleanup conditions for the PFCs. Isotope labeled PFCs were used as internal standards during the quantification process to ensure that accurate results were obtained. The method was used to analyze the total PFCs in the APM samples of winter and summer in Beijing from 2015 to 2019. Content analysis of different carbon chain length in PFCs can further aid to the understanding of the temporal trends and spatial distribution of these air born pollutants.

## 1. Experimental

### 1.1. Chemicals and materials

Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorononanoic acid (PFNA), perfluorotridecanoic acid (PFTrDA), perfluorobutanesulfonate (PFBS), perfluorohexane sulfonate (PFHxS), and perfluorooctane sulfonate (PFOS) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Perfluorooctanoic acid (PFOA) was obtained from TCI (Shanghai, China). Perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotetradecanoic acid (PFTeDA), and perfluorohexadecanoic acid (PFHxDA) were purchased from Toronto Research Chemicals (Ontario, Canada). Perfluorooctadecanoic acid (PFODA) and perfluorodecane sulfonic acid (PFDS) were purchased from A Chemtek (Worcester, USA). Three isotope labeled standards of  $^{13}\text{C}_3$ -PFBA,  $^{13}\text{C}_6$ -PFHxA,  $^{13}\text{C}_{12}$ -PFDoDA were purchased from Tokyo Chemical Industry (TCI, Shanghai, China). The remaining two isotope labeled standards of  $^{13}\text{C}_8$ -PFOA,  $^{13}\text{C}_8$ -PFOS were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All of the standards are of > 97% purity. The stock solutions of testing chemicals were made by dissolving 1 mg of the pure analytical standard in methanol, with concentrations of 10  $\mu\text{g/g}$ . HPLC Grade methanol was obtained from Merck KGaA (Darmstadt, Germany). Water, ammonium acetate (99.0%) and acetic acid (99.0%) were purchased from Thermo Fisher Scientific (Waltham, USA). All solvents were LC-MS grade. ENVI-Carb, LC-18 and LC-Si SPE sorbents were purchased from Supelclean (Bellefonte, PA, USA). Nylon filters (0.20  $\mu\text{m}$ , 13 mm) were purchased from MACHEREY-NAGEL (Düren, Germany).

Glass fiber filters (GFF), diameter 90 mm, purchased from Pall Corporation (Shanghai Branch, China), were used as sampling films. The blank sampling films were placed in a muffle furnace at 450°C and baked for 4 hr. This procedure was used to decompose any organic matter that was possibly adsorbed onto the GFF surfaces during the manufacture, transportation and storage process. We chose this condition to decompose any contaminant while maintaining the integrity of the GFF. The thoroughly cleaned sampling films were stored and equilibrated in a vacuum dryer before use.

### 1.2. Sample collection and storage

Sampling campaigns were carried out in Beijing, China from 2015 to 2019 before the COVID-19 Pandemic. A total of 60 samples were collected from the top of a six-story building (39°58'30"N, 116°25'49"E). The location of the sampling station is close to the city center with busy traffic. With schools, hospitals, residential and park areas nearby, the location is representative of an urban area in a big city. For each year, the samples were collected in December, January and February (a typical indoor heating period in the winter), and in June, July and August (a representative of non-indoor heating period in the summer). Atmospheric samples of total suspended particulate (TSP) were collected on GFFs using high volume air samplers (KC6120, Qingdao Laoshan Electronic Technology Company, China) with a flow rate of 100 L/min for 44 hr. Each

filter membrane sample was placed in an independent pre-cleaned polystyrene filter membrane-storage box, and carefully wrapped in aluminum foil to be protected from light, and stored at -20 °C before used for extraction.

### 1.3. Selective pressurized liquid extraction (SPLE)

Sample preparation, including extraction and purification, was optimized using a PLE system (ASE 350, Dionex, Thermo Scientific, USA). Extraction cells (34 mL) were loaded in turn with cellulose filter, 0.25 g ENVI-Carb, cellulose filter and GFF with TSP samples, which were cut into pieces. The PLE system and the extraction tank were cleaned in advance after being filled with gaskets. Envi-carb, an effective absorbent, was placed at the bottom of the extraction tank. SPLE was performed at 1500 psi at 120 °C with 10 min static time. The sample was extracted three times consecutively with methanol. The volume of the resulting extract solution was about 70 mL. The collected extracts were evaporated to about 1 mL, and filtered by a syringe filter (nylon, 0.20  $\mu\text{m}$ ) before injection into the LC-MS system.

### 1.4. LC-MS/MS analysis

A LC-MS/MS system (TSQ Vantage, Thermo Scientific, USA) was used for this work. Analytes were separated with an ES FluoroSep-RP Octyl column (3  $\mu\text{m}$ , 60 Å, 150\*2.1 mm). The mobile phase A was made of 400 mM ammonium acetate/water/acetic acid (1/99/0.09, V/V/V), and mobile phases B was methanol. The flow rate was 0.2 mL/min, and the column oven was kept at 25 °C. The elution started at 45% B, and the solvent was changed to 90% B in 10 min with a linear gradient. The solvent was maintained at 90% B for 3 min. The solvent was then changed to 100% B in 3 min linearly, maintained constant at 100% B for 9 min, and then returned to 45% B in 2 min and equilibrated for 10 min. The injection volume was 10  $\mu\text{L}$  using partial loop injection.

Electro spray ionization (ESI) source was operated in negative ion mode. Spray voltage, capillary temperature and evaporation temperature were set at -3000V, 250 °C and 300 °C, respectively. Data acquisition was performed in multiple reaction mode (MRM). Precursor ions, fragment ions and optimized MRM parameters including collision energy (CE) and S-Lens settings were listed in Appendix A Table S1.

## 2. Results and discussion

### 2.1. LC-MS/MS method development

In order to achieve good separations of PFCs and isomers and to improve the detection sensitivity, the component of mobile phase, type of column and pore size of packing material were optimized.

#### 2.1.1. Optimization of mobile phase

Based on the mobile phase conditions used in published literature (Llorca et al., 2009), the separation efficiency of methanol and acetonitrile as organic phase were compared. It was found that methanol was significantly better than acetonitrile under

their respective optimal separation conditions, characterized by good peak shape, narrow peak width and isomeric separations. The addition of ammonium acetate and acetic acid can help improve the peak shape and reduce retention time, and improve the ionization efficiency of PFCs. Therefore, the separation effect with aqueous mobile phase in different volume ratios as ammonium acetate (400 mmol/L) /acetic acid /water are 1/0.004/99, 1/0.09/99 and 1/0.225/99 were investigated. It was found that when ammonium acetate (400 mmol/L) /acetic acid/water (1/0.09/99, V/V/V) was used, all 16 PFCs have symmetrical peaks, good separation and optimal peak area response.

### 2.1.2. Selection of columns

Considering that PFCs contain many isomers, the aim of this optimization was to obtain the best separation of isomers in the complex matrix while reducing the possibility of interference of co-migrating species. According to the properties of PFCs, four columns with different sorbent types were used to compare the separation effects (**Appendix A Table S2**). In addition, the influence of the pore size of column packing materials on the separation effect was investigated using FluoroSep-RP Octyl column with pore sizes of 60 Å and 100 Å.

According to the chemical properties and structural characteristics of PFCs, a typical non-fluorine reversed-phase chromatographic column and three fluorine-containing reversed-phase chromatographic columns were compared in the process to optimize the separation effects of 16 PFCs. Among the four different packing materials used, XBridge@C18 column is packed with mixed silica gel particles embedded with methylene bridges in the silica skeleton. The separation of PFCs in XBridge@C18 column is mainly based on polarity (Wyndham et al., 2003). Luna 3 µm PFP(2) column is packed with silica gel, with propyl and pentafluorophenyl bonded on its surface, which has strong dipole-dipole interaction and hydrogen bonding, so that PFCs and their isomers can be retained. FluoroSep-RP Octyl column uses fluorinated octyl bonded silica gel as stationary phase, therefore it may be effective at separating PFCs and related structural isomers. The stationary phase of Epic-FDD column is perfluorinated substituted dodecyl group bonded to the surface of ultra-pure silica gel, and it should also be good at separating PFCs and related structural isomers. From the perspective of separation time, the shorter chain PFCs eluted faster than longer chain PFCs of the same functional group, and perfluorinated alkyl acids (PFAAs) eluted faster than perfluoroalkane sulfonic acids (PFSAAs) with the same carbon chain length. The order is consistent with the theory that the retention time increased with the decrease of polarity (Gao et al., 2018). The two FluoroSep-RP octyl columns and Epic FDD (3 µm 120 Å 150\*2.1 mm) are better than the other two columns in separating 16 PFCs. Good separation efficiency was shown in the separation of PFHxS and PFHpA, PFOS and PFNA. The optimized separation conditions and resulted chromatograms of five columns are compared and analyzed as demonstrated in **Appendix A Fig. S1**. Some of the PFCs cannot be separated completely by retention time because of the similar polarity, and the column directly elutes them without separation. FluoroSep-RP Octyl column showed good separation of isomers, such as linear

PFOS and its branched isomers, which can be explained as similar compatibility principle.

The columns with the same packing material but with different pore sizes were further investigated. The smaller the pore size, the better the separation efficiency. Taking 6 kinds of PFCs as representatives, including PFPeA, PFBS, PFHxS, PFHpA, PFOS, PFNA, the separation diagram of two FluoroSep-RP Octyl columns with different pore size is compared as demonstrated in **Appendix A Fig. S1**. For chromatographic columns of the same stationary phase but with a larger pore size, the peak capacity of the chromatographic column decreased. When a smaller pore sized packing was used, the analytes can fully interact with the stationary phase, thus achieving better separation. Because FluoroSep-RP Octyl (60 Å) column with fluorine-containing particles has the best peak shape and resolution, and this column was selected for the rest of the work. Representative selected reaction monitoring (SRM) chromatograms of a standard mixture of the compounds, each with 10 ng/g concentration, analyzed in MRM mode are shown in **Appendix A Fig. S2**.

### 2.1.3. Optimization of mass spectrometry conditions

MS parameters (capillary temperature, S-Lens values, collision energy, spray voltage and evaporation temperature) were optimized by flow injection analysis (FIA) for each compound to give the maximum intensity of the fragment ions obtained. It was found that the main factor affecting the signal intensity were capillary temperature and S-Lens value.

The temperature of the ion transport capillary at the inlet affects the evaporation of solvent molecules. For thermally unstable substances, too high a temperature will destroy the material structure, and too low a temperature may result in incomplete desolvation, which reduces the ion signal. Capillary temperature was optimized in the range of 200 to 400 °C. When the temperature was raised from 200 to 250 °C, the signal of PFBA, PFPeA and PFHxA signals increased, and the range of increase was 30% to 50%. When the temperature was raised further, from 250 °C to 400 °C, the signals for the PFCs decreased 40% to 80%. It seems to indicate that lower temperature leads to incomplete ionization and lower ion intensity (Du et al., 2012). When the temperature was too high, however, the substances became unstable. Therefore, 250 °C was set as the capillary temperature for the rest of the work.

S-Lens value affect the ion transmission. The optimized S-Lens of the maximum signal of each PFC was plotted according to its carbon number. It was found that as the carbon chain length increased, the optimal S-Lens value also needs to be increased (**Appendix A Fig. S3**). When the number of carbon atoms was the same, the optimal S-Lens value of PFSA was greater than that of PFAA. Other parameters, such as spray voltage, evaporation temperature, did not significantly affect the signal response, and the optimal value for the S-Lens was set at 3000 V and 300°C.

## 2.2. Optimization of SPLE

SPLE combines extraction and cleanup in one step, simplifying sample preparation, removing potential interfering matrix compounds and reducing the overall uncertainty arising from sample preparation. However, to our knowledge, SPLE has not

been used for the determination of PFCs in APM. The types and amounts of cleanup absorbent used, extraction temperature, and number of cycles used were optimized. The static extraction time was set at 10 min to maintain contact between the analytes and the solvent. The collected samples of APM in glass fiber filter were used in the optimization process. In the process of optimizing purification parameters, such as adsorbent type and adsorbent content ratio, considering that blank samples are almost impossible to obtain, 16 PFCs were added to relatively low-content samples, and the original PFCs content of the sample was deducted to obtain the final results. Detailed optimization was described in the SI, also shown in **Appendix A Fig. S4**. It was determined that ENVI-Carb, 0.25 g, was used as the absorbent for sample cleanup. All the extractions were performed at 120 °C under 1500 psi (103.4 Bar) with 60% flush volume, and the number of extraction cycles were set at 3.

### 2.3. Investigation of source of contamination

PFCs are widely used in all aspects of life and inevitably exist in the laboratory environment, which make it essential to take strict measures to avoid background contamination.

#### 2.3.1. Investigation and control of solvent background

The reagent used is the first to be concerned in pollution control. The content of PFCs in HPLC Grade methanol from different companies was investigated. Methanol (100 mL) purchased from different companies were condensed in a steam rotary dryer to 500  $\mu$ L and analyzed. It was found that the content of 16 PFCs in HPLC Grade methanol was lower than the detection limit. Considering the amount of methanol used in the detection process or pretreatment process is much lower than 100 mL, the content of perfluorocompounds in methanol can be neglected.

Different types of water were investigated. Milli-Q water prepared in the lab (Millipore, MA, USA), and LC-MS Grade water purchased from Thermo Fisher Scientific were used in the mobile phases, and the corresponding water mixed with methanol (V/V, 1:1) were injected as the sample in LC-MS. The characteristic ions of 16 PFCs were extracted from the selected ion chromatogram, and their baseline signals were analyzed. If other conditions were the same, the high baseline signal represented the high content of PFCs in the corresponding type of water, which is a large proportion in the mobile phase. The instrument limit of detection (LOD) and limit of quantification (LOQ) of 16 PFCs with different types of water as mobile phase were compared in **Appendix A Table S3**. The most prominent contaminant is PFUnDA. It can be seen that the LOD and LOQ of the instrument can be improved by 1 to 5 times by using LC-MS Grade water.

Attention should be given to the cleaning of the injection system. For example, methanol with good solubility in PFCs should be used as the needle washing solution, and the volume of the needle washing solution should be 2 to 3 times more than the volume used for injection. In addition, bottles used to contain mobile phase and needle washing liquid should be thoroughly rinsed with methanol and then sealed before use. Before each injection, blank solvent should be used

to condition the system, and the sample should only be determined after observing no interference peaks from the system.

#### 2.3.2. Investigation and control of background in the PLE process

The possibility of exogenous contamination introduced by PLE and rotary evaporation was investigated.

Methanol (100 mL) was used to clean the rotary evaporation system, and then rotary evaporated to 500  $\mu$ L. The PFC contents was measured, and the process repeated. When the measured PFC values approached a constant, this value was considered the background value that cannot be eliminated by cleaning the rotary evaporation system. The cleaning process was repeated for 7 times until the variety and content of PFCs gradually reduced to a stable value. It was found that PFOA and PFOS were the main pollutants, and the average contents were 0.092 ng and 0.070 ng, respectively.

After thoroughly cleaning the PLE system and the extraction tank with fresh methanol for three times, the pretreated sampling membrane was filled, and then the blank sampling membrane was extracted according to the method in Section 2.3. It was found that six PFCs, including PFOA, PFOS, PFNA, PFTeDA, PFTeDA and PFHxDA, were present, and the average content of the six PFCs ranged from 0.02 ng to 0.24 ng per 100 mL of methanol. Subsequent results for pretreatment experiments were all with the blank reference values deducted.

### 2.4. Adsorption of PFCs on glass

Glass materials may adsorb PFCs (Lee et al., 2018). Because glassware will inevitably be used in the experiment, the possible adsorption of PFCs on glass was investigated. The mixed standard solution of 10 ng/g was divided into sealed brown glass sample bottles, and stored in a refrigerator at 4 °C, away from light. The newly prepared standard solution in polypropylene sample bottles was used as calibration solution. The sample solutions were kept in glass vials for 0, 1, 4, and 10 days, then the concentrations of PFCs were determined. The trends of concentrations of 11 PFCs are shown in **Appendix A Table S4** and **Fig. S5**. It was shown that with the prolonged storage time, the concentrations of sulfonic acids and long-chain PFCs were not significantly changed, while the concentration of short-chain PFCs shows a downward trend with the number of days, and the reduction ranges from 6.3% to 16.9%. Therefore, glass containers should not be used for PFC analysis because the adsorption was significant.

### 2.5. Investigation of loss in rotary evaporation

Because PFCs have certain volatility, the effect of using rotary evaporation was explored (**Appendix A Fig. S6**). Standard solution was made with a concentration of 0.3 ng/g. Standard solutions of 60 mL aliquot were evaporated to 800  $\mu$ L, 400  $\mu$ L, near dryness, and complete dryness, respectively. It can be seen from **Appendix A Table S5** that when the 600 mL sample was rotary evaporated to 400 to 800  $\mu$ L, the recovery was 80% to 120%. With further rotary evaporation, the recovery of many PFCs was reduced, with shorter-chain perfluorocarboxylic acids such as PFBA and PFPeA being the most significant.

**Table 1 – Linearity, MDLs and MQLs of PFCs.**

Compounds	Internal standard	Calibration curve 0.1–100 ng/g	R <sup>2</sup>	MDL (ng/g)	MQL (ng/g)
PFBA	<sup>13</sup> C3-PFBA	$y = 1.4257x + 0.0206$	1	0.28	0.93
PFPeA	<sup>13</sup> C3-PFBA	$y = 0.5261x - 0.008$	1	0.19	0.64
PFHxA	<sup>13</sup> C6-PFHxA	$y = 0.8211x - 0.0132$	0.9998	0.48	1.6
PFOA	<sup>13</sup> C8-PFOA	$y = 0.8144x + 0.0241$	1	0.030	0.099
PFNA	<sup>13</sup> C8-PFOS	$y = 1.7601x - 0.0283$	0.9996	0.075	0.250
PFDA	<sup>13</sup> C8-PFOS	$y = 1.5298x - 0.1325$	0.9990	0.034	0.11
PFUnDA	<sup>13</sup> C12-PFDoDA	$y = 1.0089x + 0.0451$	0.9998	0.034	0.11
PFDoDA	<sup>13</sup> C12-PFDoDA	$y = 0.731x + 0.0196$	1	0.039	0.13
PFTyDA	<sup>13</sup> C12-PFDoDA	$y = 0.6054x + 0.0136$	1	0.027	0.089
PFTeDA	<sup>13</sup> C12-PFDoDA	$y = 0.5489x + 0.0096$	1	0.017	0.057
PFHxDA	<sup>13</sup> C12-PFDoDA	$y = 0.2764x + 0.0065$	0.9997	0.054	0.180
PFODA	<sup>13</sup> C12-PFDoDA	$y = 0.2018x - 0.0789$	0.9952	0.27	0.89
PFBS	<sup>13</sup> C3-PFBA	$y = 0.7054x + 0.0487$	0.9996	0.006	0.020
PFHxS	<sup>13</sup> C6-PFHxA	$y = 0.5692x + 0.048$	0.9994	0.014	0.048
PFOS	<sup>13</sup> C8-PFOS	$y = 0.6486x + 0.0072$	1	0.006	0.020
PFDS	<sup>13</sup> C8-PFOS	$y = 0.5674x - 0.0254$	0.9995	0.046	0.15

MDLs: Method detection limits, MQL: Method quantification Limit.

PFCs: Perfluorinated compounds.

PFBA: Perfluorobutanoic acid, PFBS: perfluorobutanesulfonate, PFPeA: perfluoropentanoic acid, PFHxA: perfluorohexanoic acid, PFHxS: perfluorohexane sulfonate, PFOA: Perfluorooctanoic acid, PFOS: perfluorooctane sulfonate, PFNA: perfluorononanoic acid, PFDA: Perfluorodecanoic acid, PFDS: perfluorodecane sulfonic acid, PFUnDA: perfluoroundecanoic acid, PFDoDA: perfluorododecanoic acid, PFTyDA: perfluorotridecanoic acid, PFTeDA: perfluorotetradecanoic acid, PFHxDA: perfluorohexadecanoic acid, PFODA: Perfluorooctadecanoic acid.

Therefore, it is concluded that the samples should not be rotary evaporated to less than 400  $\mu$ L in the analytical process.

## 2.6. Method validation

### 2.6.1. Linearity, method limit of detection, and method limit of quantification

Isotope labeled standards were used to test the linearity of calibration curves of the 16 PFCs (Appendix A Table S6). The standard solutions were prepared in methanol by weight. The concentration of 16 PFCs ranges from 0.1 to 100 ng/g. With serial dilution, the concentrations were made to 0.1, 0.5, 1, 5, 10, 20, 50, 100 ng/g. The concentrations of internal standards were 10 ng/g. The concentration ratio of PFCs to the corresponding internal standard was used as the X axis, and the peak area ratio was used as the Y axis to establish a standard curve. Regression coefficients ( $R^2$ ) of the calibration curve for all target PFCs were higher than 0.995, indicating that all 16 PFCs have a good linear response in the concentration range of 0.1 to 100 ng/g, and this method can be used for the quantitative determination of all 16 PFCs studied. The method detection limits (MDLs) and the method quantification Limit (MQLs) were determined when the lowest concentration detectable with a signal-to-noise ratio (S/N) of 3 and 10, respectively. The MDLs were in the range of 0.006 to 0.48 ng/g (Table 1), and the MQLs were in the range of 0.020 to 1.6 ng/g. The MDLs and MQLs of this method are comparable or better than those reported in the literature (Tian et al., 2018; Zhou et al., 2021).

### 2.6.2. Trueness and precision

Matrix spiked recovery experiment was used for accuracy and precision evaluation. Standards of 10 ng/g, 50 ng/g and 100 ng/g levels were spiked to TSP samples (Appendix A Table S7). The analysis was conducted in triplicate in three different

days. For most of the PFCs the recoveries were in the range of 82.9% to 118.5%. The intra-day and inter-day RSDs were from 1.72% to 7.64% and 1.32% to 7.04%, respectively.

Compared to traditional PFCs extraction methods, the SPLE method showed higher and more reliable recovery. For example, Lin et al. (2020) reported recoveries between 69% and 118% by mechanical shaking. And the recoveries between 31% and 175% were achieved with only ultrasonic extraction pretreatment (Zhou et al., 2021). The improvement stems from the more effective extraction efficiency and more effective sample cleanup of SPLE. In addition, because of the strict control of every single step, with the knowledge of all possible contamination sources, PFC contamination from the laboratory environment is eliminated. The method reported in the work is clearly more reliable and with better reproducibility (Zhang et al., 2016; Lin et al., 2020).

## 2.7. Method application

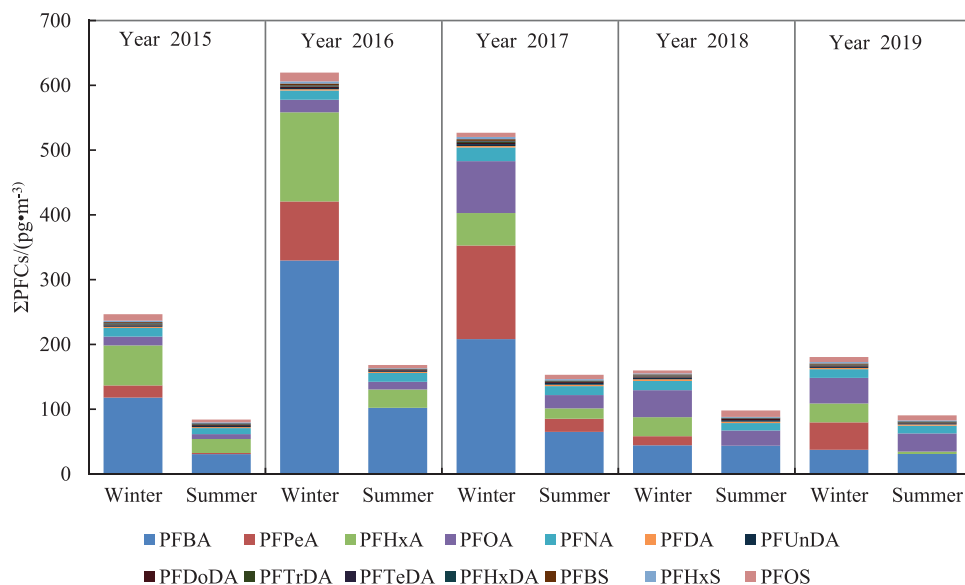
The developed method was used for PFCs content determination in TSP samples collected in the winter and summer months of 2015 to 2019 in Beijing (6 samples per year). Fourteen PFCs including PFBA, PFPeA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTyDA, PFTeDA, PFHxDA, PFBS, PFHxS and PFOS were detected in samples of both summer and winter. The data are shown in Table 2.

As shown in Fig. 1, PFCA contents were much higher than those of PFSA. In 2015, air concentrations of total PFCs ranged from 57 to 104  $\text{pg}/\text{m}^3$  in the summer months of June, July, and August, and from 72 to 429  $\text{pg}/\text{m}^3$  in the winter months of December, January (2016), and February (2016). In 2016, air concentrations of total PFCs ranged from 79 to 311  $\text{pg}/\text{m}^3$  and 314 to 1099  $\text{pg}/\text{m}^3$ , respectively, in the summer and the winter. Over the whole sampling campaign in 2017, air concentrations

Table 2 – PFCs profiles in TSP samples in Winter and Summer of year 2015~2019 (pg/m<sup>3</sup>)

Compounds	Winter (year 2015)		Summer (year 2015)		Winter (year 2016)		Summer (year 2016)		Winter (year 2017)	
	average	ranges	average	ranges	average	ranges	average	ranges	208	18~537
PFBA	118	28~340	31	8.1~47.6	329	21~725	102	37~219	145	85~224
PFPeA	18	ND~44	1.6	ND~9.8	91	16~298	ND	ND	50	5~137
PFHxA	62	15~126	22	5.3~60.0	137	45~193	28	11~49	80	17~204
PFOA	14	7.7~20.2	7.4	5.5~10.0	19.6	12~29	12	9.4~13.7	21	15~29
PFNA	13.4	8.5~23.4	9.3	7.6~10.5	14	12~24	14	11~17	2.3	1.3~3.1
PFDA	1.7	1.1~2.4	1.6	0.8~2.2	1.9	0.9~3.2	1.7	1.0~2.8	3.0	2.0~4.3
PFUnDA	2.0	1.0~3.3	1.9	1.3~2.7	1.9	1.4~3.0	1.8	1.0~2.5	1.8	1.3~2.3
PFDoDA	1.5	0.9~1.9	1.6	0.7~2.4	1.8	1.2~3.0	1.6	0.8~2.8	1.4	1.2~1.7
PFTyDA	1.0	0.5~1.5	1.1	0.5~2.0	0.8	0.2~2.0	0.7	0.4~0.8	0.8	0.6~1.2
PFTeDA	0.8	0.3~1.4	0.9	0.4~1.7	0.5	0.1~0.7	0.5	0.3~0.8	0.9	0.6~1.6
PFHxDA	0.8	0.4~1.4	0.5	0.3~0.8	0.9	0.4~1.9	0.5	0.3~0.8	ND	ND
PFODA	ND	ND	ND	ND	ND	ND	ND	ND	208	18~537
PFBS	1.2	ND~2.8	ND	ND	3.0	ND~5.6	ND	ND	3	0.7~6.2
PFHxS	2.3	ND~4.3	1.3	0.6~2.2	3.1	1.5~5.7	0.6	ND~2.2	3.4	2.4~5.2
PFOS	10	2.3~23.0	4.3	2.6~5.8	14	2.9~25.0	5.0	2.5~8.2	6.6	4.1~10.2
PFDS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total PFCs	247	73~429	84	58~104	620	315~1100	168	79~311	526	3889~816
Compounds	Summer (year 2017)		Winter (year 2018)		Summer (year 2018)		Winter (year 2019)		Summer (year 2019)	
	average	ranges	average	ranges	average	ranges	average	ranges	average	ranges
PFBA	65	8~124	44	21~77	44	ND~173	38	15~125	31	9~112
PFPeA	20	ND~89	14	ND~27	ND	ND	42	16~92	ND	ND
PFHxA	16	ND~30	29	3~73	ND	ND	29	6~56	4	ND~14
PFOA	21	14~28	41	11~137	23	11~41	40	19~88	28	19~45
PFNA	14	12~162	14	13~16	12	9~13	13	10~19	12	10~13
PFDA	2.1	1.5~3.4	2.8	1.1~10.2	2.3	1.6~4.2	2.1	1.5~3.2	1.8	1.1~2.2
PFUnDA	2.8	2.1~3.5	2.4	2.0~2.9	2.4	2.1~2.6	1.9	1.6~2.1	1.8	1.3~2.3
PFDoDA	1.5	1.2~2.2	1.6	1.3~1.9	1.7	1.3~2.5	1.3	1.1~1.6	1.3	1.0~1.5
PFTyDA	1.0	0.6~1.3	0.7	0.7~0.9	0.9	0.5~1.5	0.7	0.6~0.8	0.8	0.4~1.2
PFTeDA	0.6	0.5~0.8	0.5	0.5~0.6	0.6	0.4~0.9	0.5	0.4~0.7	0.6	0.5~0.9
PFHxDA	0.5	0.3~0.7	0.8	0.7~0.9	0.5	0.5~0.7	0.7	0.5~0.8	0.5	0.4~0.7
PFODA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFBS	0.2	ND~1	1.4	ND~3.9	ND	ND	1.7	ND~5.4	ND	ND
PFHxS	2.1	ND~4.3	1.6	0.6~2.9	1.2	0.9~1.4	2.2	1.2~4.7	1.3	0.9~1.6
PFOS	6.6	4.3~8.3	4.4	3.3~7.1	9.9	6.4~13.2	7.9	3.9~19.3	7.9	5.8~9.7
PFDS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total PFCs	153	90~286	160	77~266	98	42~237	181	108~353	91	64~194

TSP: total suspended particulate. ND: Not Detected



**Fig. 1 – PFCs profiles in TSP samples in Winter and Summer of year 2015 to 2019. PFBA: Perfluorobutanoic acid, PFPeA: perfluoropentanoic acid, PFOA: Perfluorooctanoic acid, PFHxA: perfluorohexanoic acid, PFNA: perfluorononanoic acid, PFDA: Perfluorodecanoic acid, PFUnDA: perfluoroundecanoic acid, PFDODA: perfluorododecanoic acid, PFTrDA: perfluorotridecanoic acid, PFTeDA: perfluorotetradecanoic acid, PFHxDA: perfluorohexadecanoic acid, PFBS: perfluorobutanesulfonate, PFHxS: perfluorohexane sulfonate, PFOS: perfluorooctane sulfonate.**

of total PFCs in the summer and winter ranged from 90 to 286  $\text{pg}/\text{m}^3$  and 338 to 815  $\text{pg}/\text{m}^3$ , respectively. Similarly, in 2018, air concentrations of total PFCs ranged from 42 to 236  $\text{pg}/\text{m}^3$  and 76 to 266  $\text{pg}/\text{m}^3$ , respectively, in the summer and winter. In 2019 (to February 2020), the concentrations were 63 to 193  $\text{pg}/\text{m}^3$  and 107 to 353  $\text{pg}/\text{m}^3$ , respectively.

Among PFCs, PFBA, PFPeA, PFHxA, PFOA, PFNA, PFBS, PFHxS, PFOS were the major homologues, in which PFBA has the highest concentration. The PFC composition in ambient air particulates measured in this study showed a similar distribution to that has been found in previous literature (Zhang et al., 2016; Westerdahl et al., 2009; Kim and Kannan, 2007; Shoeib et al., 2006). The content of short-chain compounds was relatively high, showing a trend of increasing at first and then decreasing, and showing obvious seasonal differences. The content of long-chain compounds was low, which was roughly maintained at a low concentration level. The total content was the highest in 2016 and 2017. More details are summarized in Table 3.

The PFC levels may be related to emission sources, industrial distribution, climate and regulation changes in Beijing and the neighboring Provinces (Liu et al., 2015). The sources of PFCs in the environment can be divided into direct sources and indirect sources. Direct sources refer to the direct discharge of gaseous industrial waste into the atmosphere during the production and use of PFCs, which includes the use of fluorine-containing products, the production and use of salts of PFCs, the use of fluorine-containing polymers (such as polytetrafluoroethylene, PTFE), especially the use of aqueous film-forming foams, and incineration of garbage. The indirect sources were mainly from the migration of PFCs by atmospheric motion and degradation of the precursor substances,

which is considered the most important influencing factor for the high content of short-chain compounds. Neighboring provinces of Beijing, such as Hebei and Shandong have many manufacturing enterprises with activities associated with the production or the emission of PFCs, such as fluoride production, and leather, textile and paper industries (Zhang et al., 2016). From studying the 16 PFCs in atmospheric particulates matter in the 5-year period, it can be seen that the content of long-chain PFCs from direct sources were much lower than those of short-chain PFCs, which was related to the production and use of PFCs in China in the period when samples were collected. In recent years, the production and use of PFCs have been restricted. In traditional industry, the most widely used PFCs are PFOA and PFOS with a carbon chain length of 8 (Paul et al., 2009). After PFOS and PFOA were listed in Stockholm Convention (Groffen et al., 2019), PFCs with short carbon chain, which supposed to be less toxic, were gradually used to replace the production and use of C8 PFCs. Different industry emitted PFCs of different characteristics. For example, PFOA, PFHxA, PFBA, and PFPeA are mainly discharged by fluorination factory, leather, textile and paper industry. Long-chain compounds, PFTrDA and PFHxDA have been found in fast food packaging, and metallurgy, electronics, paints and coatings, plastics and other industries.

According to previous research (Xu et al., 2019), the heavy pollution accumulation stage and non-pollution period in autumn and winter in 2016 and 2017 affected the air mass direction and trajectory in Beijing. The air mass transport trajectories affecting Beijing near the ground in autumn and winter mainly include northwest, west, southwest and southeast. The air flow from the southeast starts in eastern Hebei, reaches Shandong via Bohai Sea, and then transmits to Beijing



**Table 3 – Trends and sources of PFCs in TSP samples in winter and summer of year 2015–2019.**

Compounds	Trends in the five years	The year with the highest concentration	Content level	Seasonal variation difference	Pollution source
PFBA	Increasing at first and then decreasing	2016	High	Obvious in 2015-2017	Direct source/indirect source
PFPeA	Increasing at first and then decreasing	2017	High	obvious	Direct source/indirect source
PFHxA	Increasing at first and then decreasing	2016	High	obvious	Direct source/indirect source
PFOA	Increasing at first and then decreasing	2017	High	obvious	Direct source/indirect source
PFNA	Increasing at first and then decreasing	2017	Medium	obvious	Direct source/indirect source
PFDA	Maintain a low content level below 5 pg/m <sup>3</sup>	2018	Low	Not obvious	Direct source
PFUnDA	Maintain a low content level below 5 pg/m <sup>3</sup>	2017	Low	Not obvious	Direct source
PFDoDA	Maintain a low content level below 5 pg/m <sup>3</sup>	\	Low	Not obvious	Direct source
PFTrDA	Maintain a low content level below 5 pg/m <sup>3</sup>	2017	Low	Not obvious	Direct source
PFTeDA	Maintain a low content level below 5 pg/m <sup>3</sup>	\	Low	Not obvious	Direct source
PFHxDA	Maintain a low content level below 5 pg/m <sup>3</sup>	\	Low	Less obvious	Direct source
PFBS	Increasing at first and then decreasing, the concentration was lower than 5 pg/m <sup>3</sup>	2016	Low	Obvious	Direct source/indirect source
PFHxS	Increasing at first and then decreasing, the concentration was lower than 5 pg/m <sup>3</sup>	2017	Low	Obvious	Direct source/indirect source
PFOS	Increasing at first and then decreasing	2016	Medium	Obvious in 2015-2016	Direct source/indirect source

along high emission load areas such as Hengshui, Zhangzhou and Langfang. The pollutants carried by air masses passing through cities have a great influence on the formation of heavy pollution in Beijing. Because Beijing is surrounded by mountains on three sides and affected by the special terrain, air masses from the south are easily blocked by the northern mountains, and pollutants gather and accumulate continuously near the foothills, resulting in heavily polluted air mass. Therefore, the pollution level of PFCs in Beijing's atmosphere is related to the industrial production and emission in the surrounding areas. This also explains the sources of characteristic PFCs with high content, such as PFBA.

From a seasonal perspective, the concentrations of PFCs in the winter were higher than those in the summer for short chain PFCAs and PFBS. It is hot and rainy in the summer of Beijing, and roughly 80% of the annual rain fall is concentrated in the summer months of June, July and August. PFCs are easily soluble in water. Summer has the best air quality because the frequent rainfalls wash away the TSP in the atmosphere (Tang et al., 2015).

From 2017, several regulations such as "Comprehensive Emission Standard of Air Pollutants" (DB11/501-2017) were issued to reduce emissions from factories around Beijing.

For example, Hebei Province issued "Emission Standards for Volatile Organic Compounds of Industrial Enterprises", Shandong Province issued "Opinions on Strengthening Responsibility Investigation of Ecological Environment Damage", and Tianjin issued "Regulations on Prevention and Control of Air Pollution in Tianjin", which also explained that the pollution level decreased significantly in the winter of 2018. According to these regulations, the local government strengthened pollution control, which may also explain that the pollution level decreased significantly in the winter of 2018 and 2019.

### 3. Conclusions

An SPLE combined with LC-MS/MS method was developed for the first time to identify and quantify 16 PFCs in atmospheric total suspended particulate samples collected from 2015 to 2019. Due to the special physical and chemical properties of PFCs, the factors contributing to the possible contamination and/or possible loss in the experimental process were investigated for the accurate measurement of trace or ultra-trace PFCs. It allows good precision and accuracy for the determination of PFCs in APM. This method is relatively fast, simple,

with low solvent consumption and environmentally friendly. Because this method is accurate for analyzing TSP samples, it can be used to provide risk assessment from the PFC contents of TSP on the environment. The results of the 16 PFCs showed that some of the PFCs might be directly related to the extent of pollutions in the atmosphere, and might be used to reflect the effectiveness of improvement in manufacturing activities and public policy implementation. The method described should be suitable for identification and quantification of PFCs in other environmental samples such as sediment and soil.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2022.08.036.

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