

Short Communication

Perfluorinated Compounds (PFCs) in Ambient Air Particulates (PM_{2.5}, PM₁₀, TSP) in Beijing

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Abstract

The presence of perfluorinated compounds (PFCs) in ambient air particulates (PM_{2.5}, PM₁₀, and TSP) in Beijing was investigated in the current study. The results showed that PFBA, PFPeA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, and PFOS, were detected in all sizes of ambient air particulates. The concentrations of PFCs in TSP were slightly higher than those in PM₁₀ and PM_{2.5}. The concentrations of PFCs in PM_{2.5} were the lowest. The ΣPFCs contents in PM_{2.5}, PM₁₀ and TSP were 87.03-96.77, 99.82-101.41, and 118.69-141.87 ng/g, respectively. PFBA, PFPeA, and PFOA were the dominating class of PFCs in ambient air particulates.

Keywords: Perfluorinated compounds (PFCs), ambient air, particulate, industrial development zone, residential area

Introduction

Perfluorinated compounds (PFCs), with the capacity to form smooth surfaces resisting water, oil, staining, etc., had been applied in a great variety of industrial productions such as paints, surfactants, coatings, emulsifiers, fire retardants, and polymers in the past several decades [1, 2]. PFCs can be released into the environment during the use and disposal of PFCs. Previous studies found that PFCs were detected in the atmosphere, water, soil environment, and biological organisms all over the world [3-5]. The C-F bond makes the fluorocarbon chain extremely resistant to heat and chemical attack. Thus many PFCs are long-

term persistence and potential hazards, i.e., toxic or bioaccumulated, in the environment [6].

Up to now, only a few studies have examined PFCs in air. Barber et al. [7], found that PFC concentrations in air samples from northwest Europe were declining up to two orders of magnitude with decreasing degrees of urbanization. Dreyer and Ebinghaus [8] presented the distribution of PFCs in ambient air of the German North Sea and in the vicinity of Hamburg. The results showed that average total PFC concentrations in and around Hamburg (180 pg/m³) were higher than those observed in the German Bight (80 pg/m³).

Recently, some attention has been paid to ambient air particulates, because they play important roles in many environmental processes [9, 10]. Murakami and Takada [11] investigated perfluorinated surfactants in

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size-fractionated street dust. They found that concentrations of PFCs in street runoff were equal to or higher than those in wastewater influents and effluents, suggesting that street runoff contaminates waters with PFCs. PFCs can be derived from dust deposited on impervious surfaces. PFCs might accumulate in street dust and be carried by street runoff into waters. Therefore, the contributions of PFCs in ambient air particulates ($PM_{2.5}$, PM_{10} , and TSP) must be investigated.

Are there any PFCs in ambient air particulates in Beijing? In this study, we determined PFCs in ambient air particulates ($PM_{2.5}$, PM_{10} , and TSP) in Beijing from an industrial development zone and a residential area to reveal their occurrence.

Methods

Chemicals

All chemicals were of analytical grade and used as received without any further purification treatments. Organic chemicals such as perfluorobutanoic acid (PFBA, 99.5%),

perfluoropentanoic acid (PFPeA, 95%), perfluoroheptanoic acid (PFHpA, 98%), perfluorooctanoate acid (PFOA, 98%), perfluorononanoic acid (PFNA, 98%), perfluorodecanoic acid (PFDA, 98%), perfluorododecanoic acid, (PFDoA, 95%), perfluorooctane sulfonate (PFOS, 99%), perfluorohexanoic acid (PFHxA, 98%), perfluoroundecanoic acid (PFUnA, 96%), potassium perfluorobutanesulfonate acid (PFBS, 98%), and sodium perfluorohexanesulfonate acid, (PFHxS, $\geq 98\%$), were purchased from Alfa Aesar Co., Ltd, USA. Perfluorooctane sulfonamide (PFOS, 98%) and perfluorotridecanoic acid (PFTrDA, $\geq 98\%$) were purchased from Wellington Laboratories (Guelph, Canada).

Mainly the internal standard organics like quantitative standard PFCA solution/mixture ($>98\%$), $^{13}C_4$ -PFOS (MPFOS, $>98\%$), $^{13}C_8$ -PFOA (MPFOA, 99%), $^{13}C_4$ -PFBA ($>98\%$), and $^{13}C_4$ -PFDoA ($>98\%$) were obtained from Wellington Laboratories (Guelph, Canada), while the standards and stock solutions were carefully prepared using HPLC-grade methanol (99%) and then stored at 4°C in polypropylene (PP) tubes. Other chemicals such as ammonium acetate (NH_4OAc , 97%), ammonium hydroxide (50%), sodium hydroxide ($>98\%$), methanol (MeOH, $>99.9\%$), methyl-tert-butylether (MTBE, $>99\%$),

Table 1. Sampling details.

Date	Area type	Coordinates	Wind direction	Wind velocity (m/s)	Atmospheric temperature (°C)	Atmospheric pressure (kPa)	$PM_{2.5}$ ($\mu g/m^3$)	PM_{10} ($\mu g/m^3$)	TSP ($\mu g/m^3$)
07-Jun-15	Industrial development zone	N 40.2146 E 116.5509	N	2.9	28	101.2	130	148	287
	Residential area	N 39.9566 E 116.3328	N	2.0	28	101.2	130	145	280
08-Jun-15	Industrial development zone	N 40.2146 E 116.5509	N	2.4	28	99.8	127	139	266
	Residential area	N 39.9566 E 116.3328	N	2.2	28	105.2	138	145	282
09-Jun-15	Industrial development zone	N 40.2146 E 116.5509	N	2.1	29	101.6	136	155	273
	Residential area	N 39.9566 E 116.3328	N	2.5	30	101.5	144	161	298
10-Jun-15	Industrial development zone	N 40.2146 E 116.5509	S	2.8	31	102.2	135	159	293
	Residential area	N 39.9566 E 116.3328	S	2.4	32	102.2	130	162	304
11-Jun-15	Industrial development zone	N 40.2146 E 116.5509	S	3.3	30	102.3	125	154	287
	Residential area	N 39.9566 E 116.3328	S	2.6	31	102.1	133	158	293
12-Jun-15	Industrial development zone	N 40.2146 E 116.5509	S	2.7	29	101.5	133	160	310
	Residential area	N 39.9566 E 116.3328	S	2.8	29	101.8	129	164	295
13-Jun-15	Industrial development zone	N 40.2146 E 116.5509	S	2.8	30	101.6	132	163	313
	Residential area	N 39.9566 E 116.3328	S	2.8	30	101.5	130	162	305

tetrabutyl ammonium bisulfate (TBA, >97%), ammonia (50%), and acetic acid ($\geq 99.8\%$) were purchased from Alfa Aesar in the USA and Beijing Chemical Reagent Factory in China. During the experiment, all solutions were prepared using Milli-Q ultrapure water.

Sampling Sites

Daily ambient air particulate samples were taken from two sites in Beijing, one located in Shunyi industrial development zone, and another located in Dahuisi, a

Table 2. Reproducibility, recovery rates, and detection limits.

	Contents (ng/g) ^b	RSD (%)	Particulates + standards (n=4) ^a		Detection limit (ng/g)
			Recovery rates without label-recovery correction (%)	Recovery rates with label-recovery correction ^c (%)	
PM _{2.5}					
PFBA	33.24±1.2	7.8	98	86	0.1 – 0.5
PFPeA	19.22±2.6	11.2	96	81	0.1 – 0.5
PFHpA	3.33±0.4	5.6	95	84	0.1 – 0.5
PFOA	21.47±2.3	22	104.2	79.8	0.2 – 0.6
PFNA	1.42±0.3	4.5	109.5	87	0.1 – 0.5
PFDA	4.04±0.7	3.9	103.8	92	0.1 – 1.0
PFUdA	2.96±0.4	2.8	99	83	0.1 – 0.5
PFDoA	2.19±0.5	3.9	96	85	0.1 – 0.5
PFOS	4.48±0.6	7.2	99	87	0.1 – 0.5
PM ₁₀					
PFBA	37.03±4.9	23	98	83	0.1 – 0.5
PFPeA	26.55±4.2	26	102.4	89	0.1 – 0.5
PFHpA	2.41±0.8	3.0	98	80	0.1 – 0.5
PFOA	18.13± 2.2	11	96	81	0.2 – 0.6
PFNA	2.88±0.7	2.4	101	85	0.1 – 0.5
PFDA	4.97±0.8	8.5	97	89	0.1 – 1.0
PFUdA	3.18±0.5	2.6	102	83	0.1 – 0.5
PFDoA	1.72±0.5	3.4	97	81	0.1 – 0.5
PFOS	4.83±0.9	5.3	99	88	0.1 – 0.5
TSP					
PFBA	42.5±5.6	27	100	82	0.1 – 0.5
PFPeA	23.68±4.1	23	99	84	0.1 – 0.5
PFHpA	3.98±0.6	4.2	98	82	0.1 – 0.5
PFOA	27.0±3.8	19	105	89	0.2 – 0.6
PFNA	4.5±0.7	5.3	98	89	0.1 – 0.5
PFDA	5.88±0.5	6.9	99	92	0.1 – 1.0
PFUdA	6.75±0.5	5.6	103	90	0.1 – 0.5
PFDoA	3.85±0.8	7.8	97	86	0.1 – 0.5
PFOS	10.12±1.6	16	98	85	0.1 – 0.5

RSD: relative standard deviation.

^aPFC standards (40 ng/g each) were spiked into aliquots of extracts of particulates.

^bArithmetic mean±standard deviation.

^cPFOS was recovery-corrected with ¹³C₄-PFOS, PFBA was recovery-corrected with ¹³C₄-PFBA, PFDoA was recovery-corrected with ¹³C₄-PFDoA, and PFOA and other PFCs were recovery-corrected with ¹³C₈-PFOA.

residential downtown area in Beijing, China. Ambient air particulate samples were collected with quartz fiber filters (Whatman Company, UK) for 24h×7d in each sample using a high-volume air sampler (Anderson, USA) targeting PM_{2.5} and PM₁₀. A high-volume air sampler (KC-1000, Laoshan Electronic Instrument Plant, Qingdao, China) was used to collect the TSP at a flow rate of 1-1.2 m³/min for approximately 24h×7d using glass fiber filters (180 mm×230 mm, Laoshan Electronic Instrument Plant, Qingdao, China; Table 1). The ambient air particulates at two sites were collected on the same date. The weather remained dry (≤3 mm rain) for 144 h before sampling. Sieved samples were stored at 4°C before analyses.

Chemical Analyses

PFCs in ambient air particulates (PM_{2.5}, PM₁₀, and TSP) were extracted by pressurized solvent extraction (Dionex, ASE 200) with methanol at 100°C and 10.3 MPa with a flush percentage of 100% in an 11-mL cell by static extraction for 5 min. The sample was extracted twice and the extracts were combined. Fifty nanograms of injection standards were added prior to measuring to correct for volume differences. The samples were then concentrated to 1mL in a rotary evaporator. To remove interfering compounds, the samples were dissolved in 250 mL distilled water and were passed through Sep-Pak Plus tC18 cartridges (Waters) preconditioned with 30 mL methanol:acetone 1:1 (v:v). A flow rate of less than 10 mL/min was maintained. The cartridges were then washed with 20 mL methanol:acetone 1:1 (v:v) and acidified with 4M HCl to pH 2.0-2.5. The target compounds were eluted with 20 mL methanol. Concentrations of PFCs in the methanol solutions were measured using high-performance liquid chromatography (HPLC) coupled with an electrospray ionization tandem mass spectrometer (HPLC-ESI/MS/MS, API 3200; Applied Biosystems, USA) operated in negative mode. The HPLC separation was carried out by a Dionex Acclaim 120 C18 column (4.6 mm × 100 mm, 5 μm) with a gradient composition of methanol and 50 mL NH₄OAc. More details concerning the method have been given elsewhere [9, 12].

Quality Assurance and Quality Control (QA/QC)

The procedure for the QA/QC was described by Pan et al. [13]. MillQ water samples (0.02 L, n = 10) were spiked with 1 ng target standards (PFCs), treated following the same procedures as the solutions. Concentrations of all target analyses, including native and label PFCs, were quantified by using calibration curves constructed with external standards. The coefficients of determination (r²) for each calibration (5-6-point calibration) were normally higher than 0.99. Then, PFCs were corrected based on the label recovery rates. PFOS was recovery-corrected with ¹³C₄-PFOS, PFBA was recovery-corrected with ¹³C₄-PFBA, PFDoA was recovery-corrected with ¹³C₄-PFDoA, and PFOA and other PFCs were recovery-corrected with ¹³C₈-PFOA. The PFCs were extracted with

recoveries of between 79.8 and 109.5%, indicating that the SPE extraction is sufficient to support quantitative extraction. Duplicate matrix spikes were prepared for each sample. Details of reproducibility, recovery rates, and detection limits are listed in Table 2. More details concerning the QA/QC have been given elsewhere [12]. Ultrapure MilliQ water was used as a blank solution with wastewater samples. The concentrations of the samples were calibrated by the blank concentration.

Results and Discussion

PFC Concentrations in Ambient Air Particulates

In 14 kinds of PFCs, nine of them – including PFBA, PFPeA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, and PFOS – were detected in all sizes of ambient air particulates. The concentrations of PFCs in ambient air particulates are shown in Fig. 1.

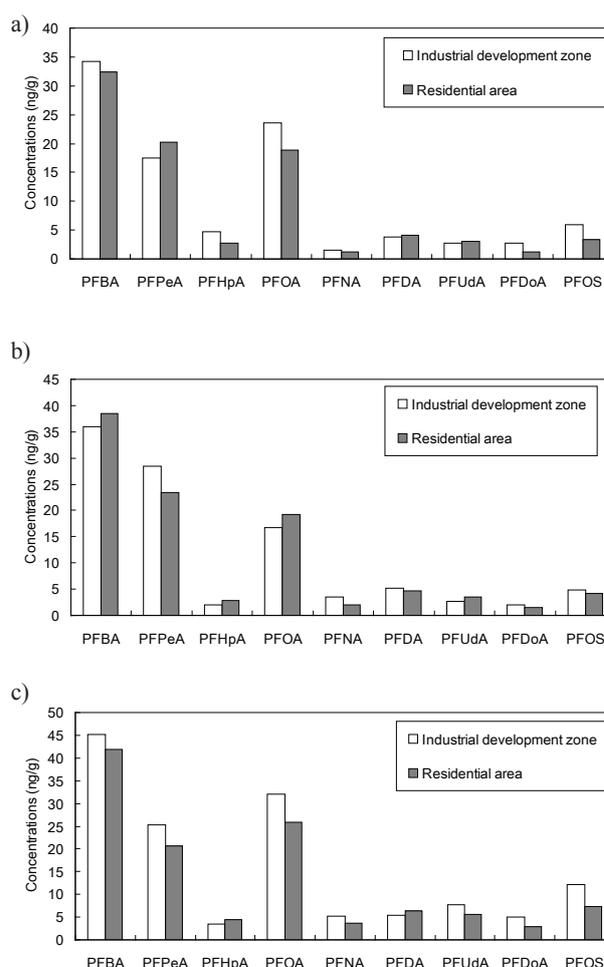


Fig. 1. Concentrations of PFCs in ambient air particulates. (a) Concentrations of PFCs in PM_{2.5} (b) Concentrations of PFCs in PM₁₀ (c) Concentrations of PFCs in TSP

In Fig. 1, the concentrations of PFCs in TSP were slightly higher than those in PM_{10} and $PM_{2.5}$. The concentrations of PFCs in $PM_{2.5}$ were the lowest. The Σ PFCs contents in $PM_{2.5}$, PM_{10} , and TSP were 87.03-96.77, 99.82-101.41, and 118.69-141.87 ng/g, respectively.

PFC Compositions in Ambient Air Particulates

Either in the industrial development zone or in the residential area in Beijing, the compositions of PFCs in ambient air particulates are identical. The contribution of single PFC to the total amount of PFCs in ambient air particulates of the residential area in Beijing is summarized in Fig. 2.

As can be seen from Fig. 2, in $PM_{2.5}$ particulates, PFBA was the dominating class of PFCs and accounted for 37%, followed by PFPeA (23%) and PFOA (22%). In PM_{10} particulates, PFBA, PFPeA, and PFOA were

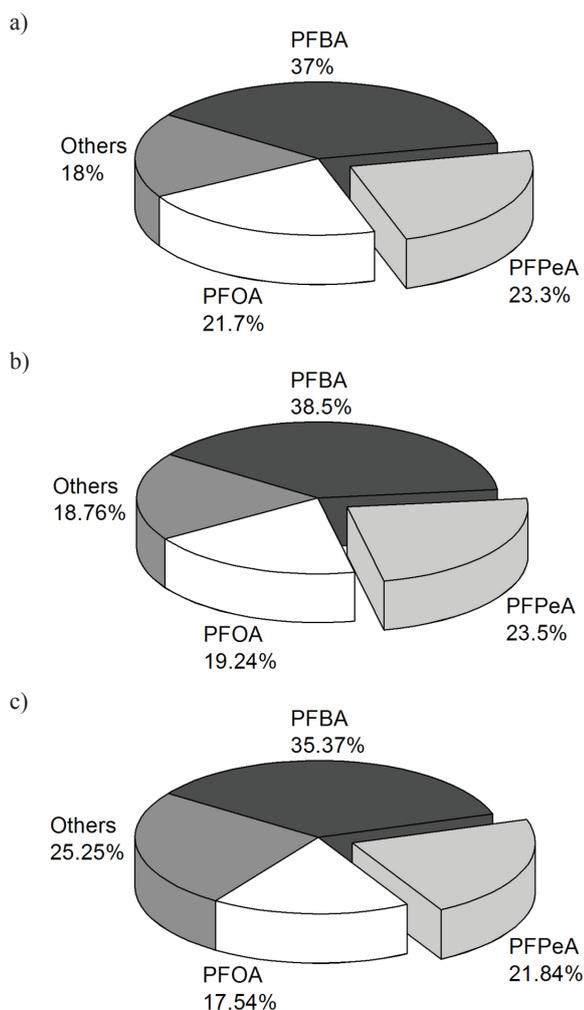


Fig. 2. The contribution of a single PFC to the total amount of PFCs in a Beijing residential area.

- (a) Single PFC to the total amount of PFCs in $PM_{2.5}$
 (b) Single PFC to the total amount of PFCs in PM_{10}
 (c) Single PFC to the total amount of PFCs in TSP

also the dominating classes of PFCs, which accounted for 38.5, 23.5, and 19.24%, respectively. Furthermore, the dominating PFCs in TSP were PFBA (35%), PFOA (22%), and PFPeA (18%).

Discussion

The PFC compositions in ambient air particulates measured in this study are similar to that found in previous research [9, 14, 15]. However, the PFC concentrations in ambient air particulates are higher than the results of other studies. The reason for this can be explained by the fact that all the monitoring processes were carried out under the condition of heavy air pollution with $PM_{2.5}$, PM_{10} , and TSP concentrations of 125-144, 154-161, and 273-298 $\mu\text{g}/\text{m}^3$, respectively. No significant differences of PFC concentrations were observed in the industrial development zone or in the residential area. In recent years the heavy pollution enterprises have been relocated to neighboring provinces, which weakens the pollution sources dramatically – even in Beijing's industrial development zone. PFC pollution in Beijing is potentially derived from the neighboring provinces, including the large amount of heavy industry in north China. Overall, currently there have been few measurements of PFCs in ambient air particulates. In addition, in the future the environmental risks of PFCs in ambient air particulates should be studied.

Conclusions

This is the first report to determine PFCs in ambient air particulates ($PM_{2.5}$, PM_{10} , and TSP) in China. We investigated PFCs in ambient air particulates from an industrial development zone and a residential area in Beijing to reveal PFC occurrence and contribution.

We have drawn the following conclusions: for 14 target PFCs, nine kinds of them (including PFBA, PFPeA, PFHpA, PFOA, PFNA, PFDA, PUnA, PFDa, and PFOS), were detected in all sizes of ambient air particulates ($PM_{2.5}$, PM_{10} and TSP). The concentrations of PFCs in TSP were slightly higher than those in PM_{10} and $PM_{2.5}$. The concentrations of PFCs in $PM_{2.5}$ were the lowest. PFBA, PFPeA, and PFOA were the dominant PFCs in ambient air particulates. No significant differences of PFC concentrations were observed in the industrial development zone or in the residential area. The PFC pollution differences between two locations are not obvious. PFC pollutions in Beijing is potentially derived from the neighboring provinces.

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References

1. PREVEDOUROS K., COUSINS I. ., BUCK R. ., KORZENIOWSKI S. . SOURCES fate and transport of perfluorocarboxylates, *Environ. Sci. Technol.* **40**, 32, **2006**.
2. SUN H. ., ZHANG X. ., WANG L., ZHANG T., LI F. ., HE N., ALDER A. . Perfluoroalkyl compounds in municipal WWTPs in Tianjin, China – concentrations, distribution and mass flow, *Environ. Sci. Pollut. Res.* **19**, 1405, **2012**.
3. CONDER J. ., HOKE R. ., DE WOLF W., RUSSELL M. ., BUCK R.C. Are PFCA's bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds, *Environ. Sci. Technol.* **42**, 995, **2008**.
4. MARTIN J.M., WHITTLE D.M., MUIR D.C., MABURY S.A. Perfluoroalkyl contaminants in a food web from lake Ontario, *Environ. Sci. Technol.* **38**, 5379, **2004**.
5. HUSET C.A., CHIAIA A.C., BAROFKY D.F., JONKERS N., KOHLER H.P.E., ORT C., GIGER W., FIELDJ. A Occurrence and mass flows of fluorochemicals in the Glatt Valley Watershed, Switzerland, *Environ. Sci. Technol.* **42**, 6369, **2008**.
6. BUTT C.M., BERGER U., BOSSI R., TOMY G.T. Levels and trends of poly- and perfluorinated compounds in the arctic environment, *Sci. Total Environ.* **408**, 2936, **2010**.
7. BARBER J.L., BERGER M.L., CHAEMFA C., HUBER S., JAHNKE A., TEMME C., JONES K. C. Analysis of per- and polyfluorinated alkyl substances in air samples from North-west Europe, *J. Environ. Monit.* **9**, 530, **2007**.
8. DREYER A., EBINGHAUS R. Polyfluorinated compounds in ambient air from ship- and land-based measurements in northern Germany, *Atmos. Environ.* **43**, 1527, **2009**.
9. WESTERDAHL D., WANG X., PAN X., ZHANG K. M. Characterization of on-road vehicle emission factors and microenvironmental air quality in Beijing, China, *Atmos. Environ.* **43**, 697, **2009**.
10. LI X. R., WANG Y. S., GUO X. Q., WANG Y. F. Seasonal variation and source apportionment of organic and inorganic compounds in PM_{2.5} and PM₁₀ particulates in Beijing, China, *J. Environ. Sci.* **25**, 741, **2013**.
11. MURAKAMI M., TAKADA H. Perfluorinated surfactants (PFSs) in size-fractionated street dust in Tokyo, *Chemosphere.* **73**, 1172, **2008**.
12. SHI Y.L., PAN Y.Y., YANG R.Q., WANG Y.W., CAI Y.Q. Occurrence of perfluorinated compounds in fish from Qinghai-Tibetan Plateau, *Environ. Int.* **36**, 46, **2010**.
13. PAN Y.Y., SHI Y.L., WANG Y.W., CAI Y.Q., JIANG G.B. Investigation of perfluorinated compounds (PFCs) in mollusks from coastal waters in the Bohai Sea of China, *J. Environ. Monit.* **12**, 508, **2010**.
14. KIM S.K., KANNAN K. Perfluorinated acids in air, rain, snow, surface runoff, and lakes: relative importance of pathways to contamination of urban lakes, *Environ. Sci. Technol.* **41**, 8328, **2007**.
15. SHOEIB M., HARNER T., VLAHOS P. Perfluorinated chemicals in the arctic atmosphere, *Environ. Sci. Technol.* **40**, 7577, **2006**.