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Determination of perfluorinated compounds (PFCs) in the fine particulate matter ($PM_{2.5}$) in China

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Abstract

Perfluorinated chemicals (PFCs) can be absorbed on fine particulate matter ($PM_{2.5}$) and used as stain, water and grease repellent in a wide range of consumer products. Among the PFCs, perfluorooctane sulfonate (PFOS) and perfluoro octanoic acid (PFOA) are widely detected in human blood and serum and are of concern due to their potential toxicity. In the present experiment, fine particulate matter ($PM_{2.5}$) from some northern (Beijing, Xian) and southern (Hong Kong, Guangzhou and Xiamen) cities of China were collected and analyzed for perfluoro butanoic acid (PFBA), perfluoro hexanoic acid (PFHxA), perfluoro octanoic acid (PFOA), perfluoro nonanoic acid (PFNA), perfluoro decanoic acid (PFDA), perfluoro undecanoic acid (PFUdA), perfluoro dodecanoic acid (PFDoA), perfluoro hexanesulfonate (PFHxS) and perfluoro octanesulfonate (PFOS) using liquid chromatography mass spectrometry (LC-MS/MS). The total PFCs ranged from 121.2 to 192.2pg/m^3, leading by Guangzhou followed by Xian, Beijing, Xiamen and Hong Koung. Among the nine measured PFCs compounds, the level of PFHxS was below the limit of detection in all the sampling cities. The other eight PFCs (PFOS, PFDoA, PFUdA, PFDA, PFNA, PFOA, PFHxA and PFBA) were detected in all the sampling locations except PFDoA in Hong Kong samples. Human exposure estimated to PFCs for adults showed PFOS as the dominant inhaled compound representing 1.59, 1.15, 1.0 and 1.0 ng/day exposure for Hong Kong, Guangzhou, Xiamen, Beijing and Xian respectively. Results from this study contribute to our understanding of exposure pathways of PFCs to humans.

Key words: Perfluorinated compounds, Fine particulate matter ($PM_{2.5}$), China, LC-MS/MS.

INTRODUCTION

Perfluorinated compounds (PFCs) are global pollutants that are known to have long environmental and biological half-life (Wallington *et al.*, 2006; Young *et al.*, 2007) and have widely been detected in humans and wildlife (Zhao *et al.*, 2011). PFCs such as perflouooctane sulfonate (PFOS) and perflourooctanoic acid (PFOA) are stable, persistent and bioaccumulative in nature and thus possesses serious public health concern. They are extensively used in lubricants, paints, cosmetics, firefighting foams and other applications (Young *et al.*, 2007). In humans, associations between PFOS or PFOA levels cause change in sperm quality (Joensen *et al.*, 2009), reduced birth weight and changes in adult thyroid hormone levels (Dallaire *et al.*, 2009). Due to the ability of PFOS and PFOA to cross the placenta they can be found in developing fetus and infants are of particular concern (Tao *et al.*, 2008). These properties of PFOS have led to its recent listing under the Stockholm Convention on persistent organic pollutants (POPs) (Wang *et al.*, 2009).

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PFCs can be transported in air and adsorbed on particulate matter ($PM_{2.5}$). A study in Keihanshin in Japan suggested that inhalation is a potential source of PFCs (PFOS, PFOA) intake (Harada *et al.*, 2005). Despite the worldwide ban on the uses of PFOS, it is still being produced and used in China. PFOS has a long half-life of 4 years in humans, suggesting that continuous exposure of PFOS could increase body burden to levels that may result in adverse health outcomes (ATSDR, 2009). Therefore, the present study was designed to measure the concentrations of PFCs in the winter dust samples collected from the northern (Beijing, Xian) and southern cities (Hong Kong, Guangzhou and Xiamen) of China using LC-MS/MS techniques.

MATERIALS AND METHODS

Air samples collection: Two northern (Beijing and Xian) and three southern (Guangzhou, Xiamen and Hong Kong) Chinese cities were selected. The samples were taken for six to eight days during the air pollution episode of haze from the end of January to the beginning of February in 2013. The $PM_{2.5}$ samples were collected on quartz fiber filter (8 inch x 10 inch) using a high-volume sampler at a flow rate of 1.05–1.16 m^3 min-1. Seven to eight air filters were collected from each sampling sites. A sampling period of ~ 24 h was adopted at all sampling sites. The filters were then wrapped in aluminum foils for further analysis in the Department of Biology, Hong Kong Baptist University, Hong Kong. The weights of filters were measured before and after the sampling procedure and were stored in desiccator cabinet at room temperature. Field blanks were also collected from each sampling site by putting the filters in the sampler without drawing air through.

Measurement of PFCs in air filters: The concentration of PFC in the $PM_{2.5}$ was determined using high-performance liquid chromatography with an electrospray tandem mass spectrometer (LCMS/MS) as previously described (Harada *et al.*, 2005; Zhao *et al.*, 2011). Briefly, one-quarter of the air filters were used for the extraction. Deuterated PFCs internal standards at the concentration of 10 ppb (sodium perfluoro-1-hexane[18O2] sulfonate, MPFHxS; sodium perfluoro-1-[1,2,3,4-13C4] octanesulfonate, MPFOS; perfluoro-n- [13C4] butanoic acid, MPFBA; perfluoro-n-[1,2-13C2] hexanoic acid, MPFHxA; perfluoro-n-[1,2,3,4-13C4] octanoic acid, MPFOA; perfluoro-n-[1,2,3,4,5-13C5] nonanoic acid, MPFNA; perfluoro-n-[1,2-13C2] decanoic acid, MPFDA; perfluoro-n-[1,2-13C2] undecanoic, MPFUdA; perfluoro-n-[1,2-13C2] dodecanoic acid, MPFDoA were added into the extracts. The homogenate was extracted by 1mL of 0.5M tetra-N-butyl ammonium hydrogen sulfate (TBA, Sigma-Aldrich, GmbH, Switzerland) solution and 2mL of 0.25 M sodium carbonate buffer in a 15-mL polypropylene tube. After being thoroughly mixed, 5mL of methyl terta-butyl ether (MTBE, Sigma-Aldrich, GmbH, Seelze) was added to the solution, and the mixture was shaken at 280 rpm for 40 minutes. After being separated by centrifugation at 3000 rpm for 10 minutes, adequate volume of MTBE (4 mL) was removed from the solution, and the process was repeated twice. The solvent was allowed to evaporate under nitrogen (N-EvapTM 112, MA, USA) and then reconstituted in 1mL solution of ammonium acetate and acetonitrile (6:4 ratios). After centrifugation, the supernatants were collected in auto sampler vials (AMB ram vial 9mm THD, Grace, USA).

LC-MS/MS system for determination of PFCs: The PFCs standards (Perfluoro-n-butanoic acid, PFBA; perfluoro-n-hexanoic acid, PFHxA; perfluoro-n-octanoic acid, PFOA; perfluoro-n-nonanoic acid, PFNA; perfluoro-n-decanoic acid, PFDA; perfluoro-n-undecanoic acid, PFUdA; perfluoro-n -dodecanoic acid, PFDoA; sodium perfluoro-1-hexanesulfonate, L-PFHxS; sodium perfluoro-1-octanesulfonate, L-PFOS) were used to obtain the standard curves.

Analysis was performed using LC/MS/MS (Agilent 1200 series, Agilent 1200 Series 6410 Triple Quad LC/MS, USA) with a sample volume of 30 µL. Sample separation was achieved in the Zorbax Eclipse plus C8 column (2.1x 100mm, 3.5 micron), using a mobile phase of 10 mM ammonium acetate/water (v/v) at a flow rate of 0.25 mL/min. The gradient profile was as follows: a linear increase from 40% to 90% acetonitrile (ACN) solution in 0-5.5 min, held at 90% for 4 min, then held at 100% for 1 min. PFCs were quantitatively analyzed by single mass mode using characteristic ions at m/z.

Quality control/quality assurance: The limit of detection (LOD) was determined as the concentration of an individual PFCs detected in a sample with a signal-to-noise ratio of 3. The concentrations of PFCs in the method blank were less than the LOD. All the results were expressed as per one fourth of air filter.

Risk assessment: Inhalation exposure (Einhal, pg/day) was calculated as published previously (Shoeib *et al.,* 2011). EInhal= C air x V air x F uptake fraction .Where C air is the concentrations of PFCs (pg/m^3) in PM$_{2.5}$, V air is the volume inhaled (m^3/day).

RESULTS AND DISCUSSION

PFC concentrations in the PM$_{2.5}$ samples: Air filters were collected from the five cities in southern (Hong Kong, Guangzhou and Xiamen) and northern (Xian and Beijing) China. The weights of PM$_{2.5}$ collected on the filters were measured (Fig. 1A). The weights of PM$_{2.5}$ per m^3 air collected in the northern cities of China were approximately 4 times higher than that of the southern cities, weighted in average of 228µg and 50µg respectively. The concentrations of PFCs in PM$_{2.5}$ per m^3 air flow of the five selected cities were shown in Fig 1B and details were listed in Table 1.

Among the nine measured PFC compounds, the levels of PFHxS in all the samples were below the limit of detection. The other 8 PFCs (PFOS, PFDoA, PFUdA, PFDA, PFNA, PFOA, PFHxA and PFBA) were detected in the samples from Guangzhou, Xiamen, Xian and Beijing, while PFDoA was not found in the Hong Kong samples (Table 1). Total PFC concentrations calculated by the summation of all PFC compounds ranged from 121.2 to 192.2 pg/m^3, leading by Guangzhou followed by Xian, Beijing, Xiamen and Hong Kong. The levels of PFCs detected in this study, were relatively higher than previous studies on PFOS contamination in ambient air from Japan (Harada *et al*., 2005; Sasaki *et al*., 2003).

PFOS was the most abundant species among the nine PFCs measured with the highest concentrations detected in most sampling sites ranging from 28.25- 99.4 pg/m^3.

However, its levels were found to be noticeable higher (> 72pg/m3) in the northern cities (Xian and Beijing) versus in all the three southern cites (< 65pg/m^3 air). In this study PFOS, PFHxA, PFBA and PFOA were predominantly measured in 5 sampling cities reflecting the very low volatility of these compounds.

Shoeib *et al.*, 2011 reported ionic PFCs in the indoor window film in Toronto with a profile dominated by PFOA, PFDA, PFNA, and PFOS which is consistent with our findings.

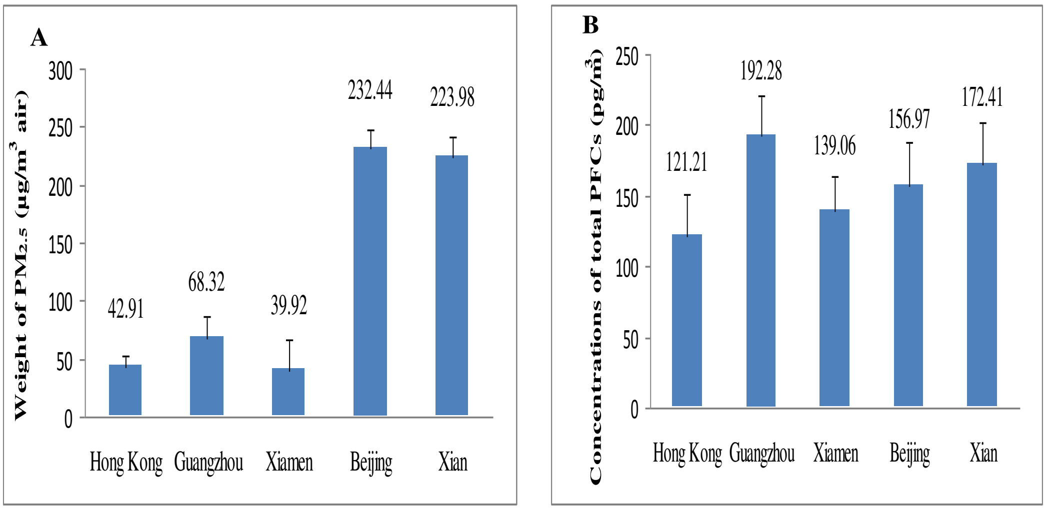

Fig 1. The weights (µg/m^3) of $PM_{2.5}$ dust in air filters (A) and the mean concentrations (pg/m^3) of total PFCs in each sampling site (B)

PFOS exhibited the highest concentration in Hong Kong with an average mean of 99.45pg/m3 which comprised 82% of the total PFC content while PFHxA, PFBA and PFOA exhibited 49, 87 and 16.81 pg/m^3 respectively for Xian, Guangzhou and Xiamen (Table 1).

PFCs concentrations of samples from northern China (164.69 pg/m^3) were higher than that from the southern cities (150.8 pg/m^3), showing the less severe pollution in the southern cities. As we did not have any direct evidence in terms of the sources of PFCs, it was believed that the traffic density (Sasaki *et al.,* 2003) might be responsible for the PFC contamination levels in the northern cities. Other possible sources of PFC emission can be found in fire extinguishers and industrial products. It was reported that PFOS was one of the ingredients in fire extinguishing media (Moriwaki, *et al.,* 2003). In addition, teflon contained PFOA is widely used in paint sealant coating, oil additives and grease manufacturing purposes (Harada *et al.,* 2005).

Table 1. Total concentrations (pg/m^3) and inhalation concentration (ng/day) of PFCs from different cities of China

Cities	Hong Kong		Guangzhou		Xiamen		Beijing		Xian	
PFC compounds	Con. (pg/m^3)	Inhalation exposure (ng/day)	Con. (pg/m^3)	Inhalation exposure (ng/day)	Con. (pg/m^3)	Inhalation exposure(ng/day	Con. (pg/m^3)	Inhalation exposure (ng/day	Con. (pg/m^3)	Inhalation exposure(ng/day
PFOS	99.45	1.59	72.39	1.15	28.25	0	74.77	1	70.78	1
PFHxS	0	0	0	0	0.00	0	0.00	0	0.00	0
PFDoA	0	0	0.36	0.00	0.33	0	1.90	0	0.36	0
PFUdA	0.84	0.01	0.36	0.00	0.41	0	2.00	0	0.43	0
PFDA	0.60	0.00	0.69	0.01	0.79	0	1.31	0	0.42	0
PFNA	2.28	0.03	2.646	0.04	2.78	0	3.96	0	3.21	0
PFOA	3.89	0.06	11.73	0.18	16.81	0	14.05	0	4.52	0
PFHxA	3.01	0.04	16.84	0.26	18.96	0	27.66	0	49.32	1
PFBA	11.12	0.17	87.23	1.39	70.72	1	31.32	1	43.37	1
Total	121.2	1.93	192.28	3.07	139.06	2	156.97	3	172.41	3

PFCs compositions in different cities of China

Hong Kong: PFOS exhibited the highest concentration in Hong Kong with an average mean of 99.45 pg/m^3 which constituted 82% of the total PFC content. Among the other PFCs, PFBA (11.12 pg/m^3), PFHxA (3pg/m^3), PFOA (3.89 pg/m^3) and PFNA (2.28pg/m^3) were also dominant which constituted 9.17, 3.21, 2.48 and 1.88% of the total PFC content respectively while PFHxS and PFDoA were found below the limit of detection (LOD) (Table 1).

Guangzhou: In Guangzhou, $PM_{2.5}$ samples were dominant with PFBA (87.23 pg/m^3) which formed 45% of the total PFC content. In contrast, PFOS (72.39 pg/m^3), PFHxA (16.84 pg/m^3) and PFOA (11.3 pg/m^3) were detected at 37.65, 8.76, 6.10% of total PFC content respectively (Table 1).

Xiamen: PFBA (70.71pg/m^3) exhibited the highest concentration followed by PFOS (28.25 pg/m^3), PFHxA (18.96 pg/m^3), PFOA (16.81 pg/m^3) and PFNA (2.77pg/m^3) respectively. Among the PFC compounds, PFBA and PFOS constituted 50.58 and 20.31% of the total PFC content respectively (Table 1).

Beijing: Among the PFCs, PFOS (74.76 pg/m^3) was most abundantly found while other PFCs were detected at relatively low abundance with PFHxS below the LOD. Among the PFC compounds, PFOS (74.76 pg/m^3), PFBA (31.31pg/m^3), PFHxA (27.65pg/m^3) and PFOA were the dominant congeners contributing to 47.6, 19.9, 17.6 and 12.08 % of the total PFC content respectively (Table 1).

Xian: PFOS exhibited the highest concentration (99.45pg/m^3) which constituted 41% of the total PFC content. PFBA (43.36 pg/m^3), PFNA (3.21pg/m^3) and PFOA (4.52 pg/m^3) were also detected in the samples with PFHxS below the LOD (Table 1).

Human exposure to PFCs by inhalation: An adult male inhale 20m^3 of air daily (Arrieta *et al.,* 2003), thus to estimate the inhalation exposure, we multiplied the PFCs concentrations with the volume of air inhaled. Accordingly, the daily intake was estimated to be 1.93, 3.07, 2, 3, and 3 ng/day for Hong Kong, Guangzhou, Xiamen, Beijing and Xian respectively (Table 1). Among the PFCs, PFOS was the dominant inhaled compound representing 1.59, 1.15, 1 and 1ng/day exposure for Hong Kong, Guangzhou, Beijing and Xian while PFOA was inhaled at 0.06 and 0.18ng/day in Hong Kong and Guangzhou respectively (Table 1).

A study in Canada reported the dietary intake of 110 ng/day for PFOS and 70 ng/day for PFOA (Tittlemier *et. al.,* 2007). In our study, we estimated that the intake of total PFCs by inhalation represented about 91% (Hong Kong), 41% (Guangzhou), 37% (Beijing) and 37% (Xian) for PFOS and for PFOA 2% (Hong Kong) and 4% (Guangzhou) of the Canadian dietary contribution.

On the contrary, another study reported (Shoeib *et al.,* 2011) around 28% of the PFCs intake by inhalation of the Canadian dietary contribution. In this study, the daily intake of PFOS in Chinese cities were higher compared to that of 10 and 100 pg/day inhalation exposure of Fukuchiyama city and Oyamazaki town of Japan (Sasaki *et al.,* 2003) respectively. Published data suggested that PFOS through inhalation was little compare to drinking water (Sasaki *et. al.,* 2003). Human exposure to PFCs via inhalation suggests that continuous exposure of PFCs could increase body burden to the levels that would result in adverse health outcomes (ATSDR 2009). However, this study will facilitate the investigations of related health effects and human monitoring data.

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