PERFLUORINATED COMPOUND LEVELS IN URBAN AIRBORNE PARTICLES
— RECENT ASPECTS IN TOKYO AREA —

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Abstract

Perfluorooctane sulfanate (PFOS) concentrations in urban particles were determined during summer and winter, 2006. The mean concentration of PFOS was 7.3pg/m^3 in July and 4.3pg/m^3 in December, respectively. And PFOS concentrations in July were higher than in December. PFOS concentrations on weekend were lower than weekdays in spite of there were no significant differences by a statistic test. On the other hand, TSP concentrations were almost similar between in July and December. Some POPs (PFOS, dinitropyrenes (DNPs), 3,6-dinitrobbenzo[e]pyrene (DNBeP), and dioxins) concentrations in size fractionated particle were determined in December. DNPs and dioxins made up the majority of particles of size <1.1um, although PFOS and DNBeP were mainly contained in particles of size >1.1um. PFOS levels in particles of size >1.1μm exceeded 90%, and DNBeP in particles of size >1.1μm amounted to over 80%.

Introduction

Perfluorooctane sulfonate (PFOS) is a member of the group of perfluorinated compounds (PFCs) which have been manufactured for more than 50 years and are widely used as surfactants, surface protectors and performance chemicals in products. These compounds have recently been detected in environmental air, surface water and in animals as well as in human serum. The Swedish Chemicals Inspectorate has proposed listing PFOS in Annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs).[1] In order to estimate human exposure to these chemicals, their environmental concentrations must be measured, despite the scarcity of existing reports on levels of airborne PFOS, which cover certain cities, such as Kyoto and Morioka [2, 3] in Japan and Hazelrigg and Manchester in England.[4]

In this study, we measured concentrations of PFOS and certain other pollutants in airborne particles in Wako, located northwest of Tokyo during the summer and winter of 2006.

Materials and Methods

Reagents**:** Methanol (pesticide residue analysis grade) and distilled water (HPLC analysis grade) were purchased from Wako Pure Chemical Industries Ltd. (Japan), while perfluorooctane sulfonate potassium salt was purchased from Strem Chemicals (USA).

Sample collection**:** The total suspended particles (TSP) were collected on a quartz fiber filter (20 cm x 25 cm, Pallflex Products Co., USA) using high volume air samplers (Shibata Scientific Technology Ltd., Japan) placed on the rooftop of the National Institute of Public Health (NIPH) building, located in Wako City, Saitama, for 3 weeks in July and December 2006. In addition, fractionated airborne particles were collected for one week in December using an Andersen high volume air sampler (Shibata Scientific Technology Ltd., Japan), which classified particles into 5 groups according to size. After being weighed, the particle samples were placed into deep frozen storage (-80 ^{o}C).

Extraction and sample treatment: Filter samples were cut into small pieces and placed into 200 mL Erlenmeyer flasks. 100 mL methanol was then added and the mixture was sonicated twice for 20 minutes. After extraction, solutions were passed through a nylon membrane filter (pore size 0.2μm, Iwaki, Japan) to remove suspended materials and insoluble particles. After removing the solvent by evaporation at room temperature under a weak nitrogen gas flow, the extracts were dissolved in 500µL solvent (methanol: 0.5mM CH_3COONH_4 aq.=1:1) for LC/MS/MS analysis.

LC/MS/MS analysis and Quantification: Analysis of PFOS was performed by an HPLC tandem mass spectrometer (LC/MS/MS), comprising an Agilent HP1100 LC system interfaced with a Micromass QII API tandem mass spectrometer operated in electrospray negative ionization mode. The analytical methods were in line with the previous report ^{5}.

Results and Discussion

Figure 1 showed the results of PFOS and TSP concentrations for the 3 week survey during the summer and winter of 2006. From figure 1, PFOS has been detected in all samples and ranged from 3.6pg/m^3 to 15.7pg/m^3 in July, and from 0.9pg/m^3 to 8.9pg/m^3 in December. Both PFOS and TSP concentrations varied during both months, although there was no link between the PFOS and TSP concentrations.

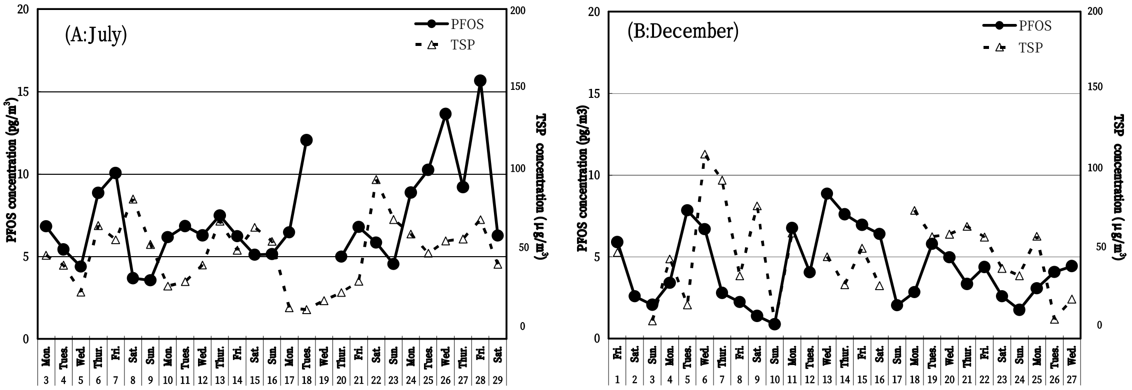

Fig. 1 PFOS and TSP concentrations in Wako-shi 2006.
A: July B: December

The statistical information for the PFOS and TSP results is shown in Table 1, which shows a comparison of the summer and winter atmospheric levels. The mean concentration of PFOS was 7.3pg/m^3 in July and 4.3pg/m^3 in December respectively. PFOS concentrations in July were higher than those in December (ratio of July/Dec. was 1.7 on their mean and 1.6 on their median), although there were no significant differences by a statistical test (Student's t-test, <t(51, 0.10)). The level of PFOS in winter season in Wako was slightly lower than that in the central area of Tokyo (Shirokane-dai, Minato Ward) in 2003 (mean: 5.7pg/m^3). On the other hand, TSP concentrations were almost similar between in July and December (ratio of July/Dec. was 1.0 on their mean values). Daily variations of PFOS concentration in July were similar to those in December, and the same applied to TSP concentrations. Goto et al.$^{6)}$ reported that the daily variation (geometric relative standard deviation) of BaP concentrations in atmosphere was 67.7% in January and 140% in July. On the other hand, the daily variation of PFOS concentrations was 22.1% in July and 48.6% in December. These values were smaller than those of BaP.

PFOS and TSP concentrations were summarized to a day of the week in Figures 2-1 and 2-2. In Figure 2-1, PFOS concentrations on weekends (Saturday and Sunday) were lower than those on weekdays (from Monday to Friday), in spite of there were no significant differences by a statistical test. But, a considerable variety of TSP concentrations were evident among every day of the week in Figure 2-2.

Table 1. Comparison of summer and winter levels in atmosphere.
(general statistic information of PFOS and TSP)

	PFOS (pg/m^3)			TSP (μg/m^3)		
	July	Dec.	July/Dec.	July	Dec.	July/Dec.
n	26	27	-	27	24	-
mean	7.3	4.3	1.7	52	51	1.0
s.d.	3.0	2.2	1.4	20	27	0.8
RSD*	41.1	51.8	-	39	52	-
max	15.7	8.9	1.8	97	113	0.9
median	6.4	4.0	1.6	54	51	1.0
min	3.6	0.9	4.1	18	9.1	1.9
geomean	6.8	3.7	1.8	48	43	1.1

*: (%)

Particle size fractionated POPs concentrations were shown in Table 2. From Table 2, DNPs and DXN made up the majority of particles of size <1.1um, although PFOS and DNBeP were mainly contained in particles of size >1.1um. PFOS levels in particles of size >1.1μm exceeded 90%, and DNBeP in particles of size >1.1μm amounted to over 80%. From these results, it was suggested that the sources and behavior of PFOS and DNBeP were different from DXN and DNP.

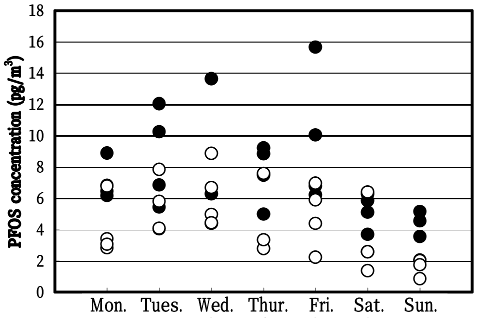

Fig. 2-1 The variation of PFOS concentrations depending on a day of the week

● July ○ December

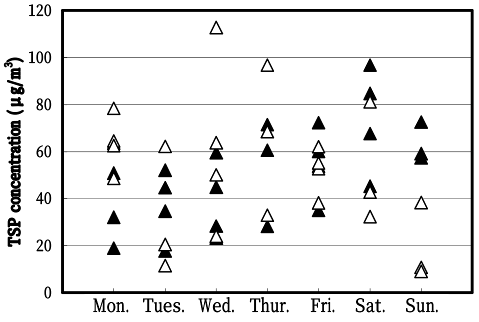

Fig. 2-2 The variation of TSP concentrations depending on a day of the week

▲ July △ December

Table 2 Particle size distribution of POPs related compounds concentrations in atmospheric air.

	particle size	PFOS [pg/m^3]		3,6-DNBeP [pg/m^3]		DNPs [pg/m^3]		DXN [pg-TEQ/m^3]	
A	>7.0um	0.98	(26%)	0.24	(17%)	0.032	(14%)	0.0028	(3.8%)
B	7-3.3um	0.77	(21%)	0.27	(19%)	0.027	(12%)	0.0036	(4.9%)
C	3.3-2.0um	0.89	(24%)	0.53	(37%)	0.033	(15%)	0.0044	(6.0%)
D	2.0-1.1um	0.74	(20%)	0.20	(14%)	0.021	(9.3%)	0.0069	(9.4%)
Back Up	<1.1um	0.35	(9.3%)	0.19	(13%)	0.114	(50%)	0.0560	(76%)
Σ		3.74	(100%)	1.43	(100%)	0.227	(100%)	0.0737	(100%)

DNBeP: 3,6-dinitrobenzo[e]pyrene.

DNPs: 1,3-, 1, 6- and 1, 8-dinitropyrenes.

DXN: PCDDs + PCDFs + coplaner PCB

Acknowledgements
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