

PERFLUORINATED COMPOUNDS IN ATMOSPHERE OF HYOGO PREFECTURE, JAPAN.

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Abstract

This study investigated perfluorinated compounds (PFCs) in the atmosphere of Hyogo prefecture, Japan. Target compounds were perfluorinated carboxylic acids (PFCA, C4-C14), perfluorinated alkyl sulfonates (PFAS, C4, C6, C8, C10), and 12 kinds of fluorotelomer compounds (FTs) such as fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAcrylates), fluorotelomer methacrylate (FTMethacrylate), fluorotelomer iodides (FTIs), and fluorotelomer olefins (FTOlefins). Air samples were collected by using a high volume air sampler at 3 sampling sites in Hyogo prefecture in August (summer) and December (winter) of 2009. Quartz micro fiber filters (QMF), poly-urethane foams (PUF), and activated carbon felts (ACF) were used for collection media. Target compounds were analyzed by using GC/MS and UPLC/MS/MS.

As a result, PFCA (C4-14), PFOS, 6:2FTOH, 8:2FTOH, 6:2FTAcrylate, 8:2FTAcrylate, 8:2FTI, and 10:2FTOlefin were detected that differed from site to site and also in each season. In addition, some PFCA were detected in both particle phase and gas phase in summer, whereas the compounds were detected in only particle phase in winter.

Introduction

Perfluorinated compounds (PFCs) as typified by perfluorinated octane sulfonate (PFOS) and perfluorinated octanoic acid (PFOA) are used in a variety of consumer and industrial applications. However, PFOS and PFOA were found to be persistent, bioaccumulative, some toxic properties. Furthermore, PFOS, PFOA and related compounds, such as perfluorinated carboxylic acids (PFCA) and perfluorinated alkyl sulfonates (PFAS), have been detected from human bloods¹, in biota², and in the environment³ from over the world. As PFCs pollution became recognized as a serious problem in the world, PFOS and PFOSF were added as persistent organic pollutants (POPs)⁴.

As reasons for the occurrence of PFCs in remote regions, several studies suggested that PFCA and PFAS can be transported over long distances by water^{5,6}. On the other hand, PFCA and PFAS were detected in the atmosphere, and the atmospheric transport is confirmed by some studies^{7,8}. Fluorotelomer compounds (FTs) such as fluorotelomer alcohols (FTOHs), are related to PFCA pollution. FTs are volatile and semi-volatile compounds which are degraded to PFCA in the atmosphere⁹. Degradation of FTs to PFCA during or after atmospheric transport reveals the contribution of FTs to the ubiquitous distribution of PFCA¹⁰. However, the facts of PFCs in the atmosphere, especially of localized pollution, are not yet fully understood.

In this study, PFCA, PFAS, and FTs in the atmosphere were investigated in urban areas of Hyogo prefecture, Japan. In addition, simultaneous analysis of PFCA, PFAS, and FTs were attempted to investigate comprehensive distribution of PFCs.

Method

Target Compounds and Sampling

The target compounds are shown in table 1. Air sampling was conducted at three sites located in the southeast of Hyogo Prefecture, Japan, in the summer and winter of 2009.

The air sample were collected by using a high volume air sampler (HV-700F, SIBATA) at the sites described above with sampling volume of approximate 1000 m³ and with flow rate of 700 L/hr. Quartz micro fiber filters (QMF, QR-100, 203×254mm, ADVANTEC), Poly-urethane foams (PUF, 80mmφ, SIBATA) and activated carbon felts (ACF, Fiber AC disk, 85mmφ, Autoprep, Showa denko) were used for collection media (Fig.1).

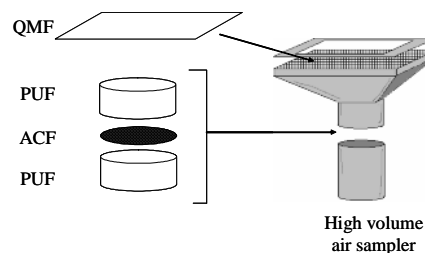


Fig.1 QMF folder and PUF folder of High volume air sampler

Table 1 Target compounds

Name	Acronym	Name	Acronym
Perfluorobutanoic acid	PFBA	1H,1H,2H,2H-Perfluorohexan-1-ol	4:2FTOH
Perfluoropentanoic acid	PFPeA	1H,1H,2H,2H-Perfluorooctan-1-ol	6:2FTOH
Perfluorohexanoic acid	PFHxA	1H,1H,2H,2H-Perfluorodecan-1-ol	8:2FTOH
Perfluoroheptanoic acid	PFHpA	1H,1H,2H,2H-Perfluorododecan-1-ol	10:2FTOH
Perfluorooctanoic acid	PFOA	1H,1H,2H,2H-Perfluorooctyl acrylate	6:2FTAcrylate
Perfluorononanoic acid	PFNA	1H,1H,2H,2H-Perfluorodecyl acrylate	8:2FTAcrylate
Perfluorodecanoic acid	PFDA	1H,1H,2H,2H-Perfluorodecyl methacrylate	8:2FMetacrylate
Perfluoroundecanoic acid	PFUnDA	1H,1H,2H,2H-Perfluorohexyl Iodide	4:2FTI
Perfluorododecanoic acid	PFDoDA	1H,1H,2H,2H-Perfluorooctyl Iodide	6:2FTI
Perfluorotridecanoic acid	PFTTrDA	1H,1H,2H,2H-Perfluorodecyl Iodide	8:2FTI
Perfluorotetradecanoic acid	PFTeDA	1H,1H,2H-Perfluoro-1-dodecene	10:2FTOlefin
Perfluorobutane sulfonate	PFBS	1H,1H,2H-Perfluoro-1-tetradecene	12:2FTOlefin
Perfluorohexane sulfonate	PFHxS		
Perfluorooctane sulfonate	PFOS		
Perfluorodecane sulfonate	PFDS		

Sample analysis

QMF and PUF were used for PFCAs and PFASs analysis. QMF and PUF were spiked with mass labeled PFCAs and PFASs mixture (MPFAC-MXB, Wellington) as cleanup spikes, and the each media was set into a 100mL glass tube. The glass tubes were filled with 25% ammonium / methanol, 1:100, and the medias were ultrasonic extracted for 15 min. The extracts were transferred to beakers, and the extraction process was repeated 2 times. The extracts were filtered with filter papers (5A, 125mm, ADVANTEC), and concentrated under nitrogen stream to 1 mL. $^{13}\text{C}_8$ PFOA (CIL) was spiked to the concentrated solutions as a syringe spike, and the final solutions were analyzed using UPLC/MS/MS.

ACFs were used to FTs analysis. ACFs were spiked with mass labeled 6:2FTOH, 8:2FTOH, and 10:2FTOH (Wellington) as clean up spikes, and the extracts was conducted with ethyl acetate using Accelerated Solvent Extractor (ASE200, Dionex). The extracts concentrated under nitrogen stream to 1 mL. The concentrated solutions were added with 1H, 1H-Perfluoro-1-nonanol (8:1FA) as a syringe spike, and were analyzed using GC/MS.

Table 1 analysis condition of LC/MS/MS and GC/MS

LC conditions		GC/MS conditions	
Instrument	: ACQUITY UPLC (waters)	Instrument	: Agilent 6890N/JEOL JMS-K9
Column	: UPLC BEH C18 2.1×50mm	Column	: J&W Sci. DB200 30m×0.25 I.D.(0.25μm)
Retention gap Column	: UPLC BEH C18 2.1×100mm	Injection volume	: 2μl(Splitless)
Mobile Phase	: A : 10mM Ammonium Acetate aq B : Acetonitrile	Injection port temp	: 220
Gradient	: 0.0 8.0min B : 1 95% 8.0 8.1 B : 95 1%	Column oven temp	: 40 (5min) 10 /min 150 (0min) 20 /min 280 (15min)
Flow rate	: 0.3 mL/min	Carrier gas	: Helium (Flow rate 1mL/min)
Column temp.	: 50	Ion source temp	: 230
Injection volume	: 5μL	Interface temp	: 200
MS conditions		Ionization method	: EI
Instrument	: ACQUITY TQD (waters)	Ionization energy	: 70ev
Ionization Mode	: ESI(-)	Mode	: SIM
Source temp	: 120		
Desolvation temp	: 300		
Capillary voltage	: 2 kV		
Cone gas flow	: 20 L/Hr		
Desolvation gas flow	: 800 L/Hr		
Collision Gas Flow	: 0.1 mL/Min		

Results and Discussion

Breakthrough and Recovery experiments

The breakthrough experiments of PFACs and PFASs were conducted by spiking MPAC-MXA on to QMF to determine which medias would collect PFACs and PFASs. Each media, including ACF, was extracted. Also, the similar examinations about FTs were conducted. As results, it was confirmed that PFCAs and PFASs were

collected by QMF and upper PUF, and FTs were collected by ACF. Therefore, QMF and PUF were used to PFCAs and PFASs analysis, and ACF was used to FTs analysis in this study.

The recovery experiments were conducted by spiking PFASs and PFCAs mixture (PFAC-MXB) on to QMF and FTs mixture on to PUF. Spiked medias and unspiked medias were set into two high-volume air samplers respectively, and were aerated. The absolute recovery rates were between 29%(4:2FTI) and 125%(PFDS). It was observed that FTs and PFCAs, especially those with shorter carbon chain length, were lost during an analytical process. The losses during pretreatments were correct by internal standard method using the cleanup spikes.

Concentrations of PFCs in Atmosphere of Hyogo Prefecture

Fig.1 shows the results of the target compounds distribution in atmosphere at sampling point. FTs at sampling point C in winter were not analyzed. In this study, the compounds collected by QMF were assumed to be in the particle phase, and the compounds collected by PUF and ACF were assumed to be in the gas phase.

As a result of Fig 1, PFCAs(C4-14), PFOS, 6:2FTOH, 8:2FTOH, 6:2FTAcrylate, 8:2FTAcrylate, 8:2FTI, and 10:2FTOlefin were detected that differed from site to site. The concentration of PFCAs, especially PFOA, at sampling point C in summer was higher than the other sampling points, which is more distinctive in summer, when concentration level is relatively higher. In other our studies, PFHxA were detected in high concentration in the river near sampling point C. Sampling point C and the river of PFCAs distribution pattern were different. According to the previous results, it was suggested that the main pollution source of PFCAs in atmosphere at sampling point C was different from that in the river. Moreover, various FTs were detected at sampling point B and C in summer. Detected FTs were intermediates in the synthesis of fluorinated polymers. It was also confirmed in our previous study¹²⁾ that these FTs were remained as impurities in fluorinated polymer-based oil and water repellents. It appears that the distribution of FTs in Sampling point B and C reflected the effect of some sources.

The Concentrations of PFCs were also different in each season. The concentrations of PFCAs in winter were low compared with those in summer. In addition, some PFCAs were detected in the particle phase and the gas phase in summer, whereas the compounds were detected in particle phase in winter (Fig.2). The difference in concentrations and phases of PFCAs can be attributed to temperature.

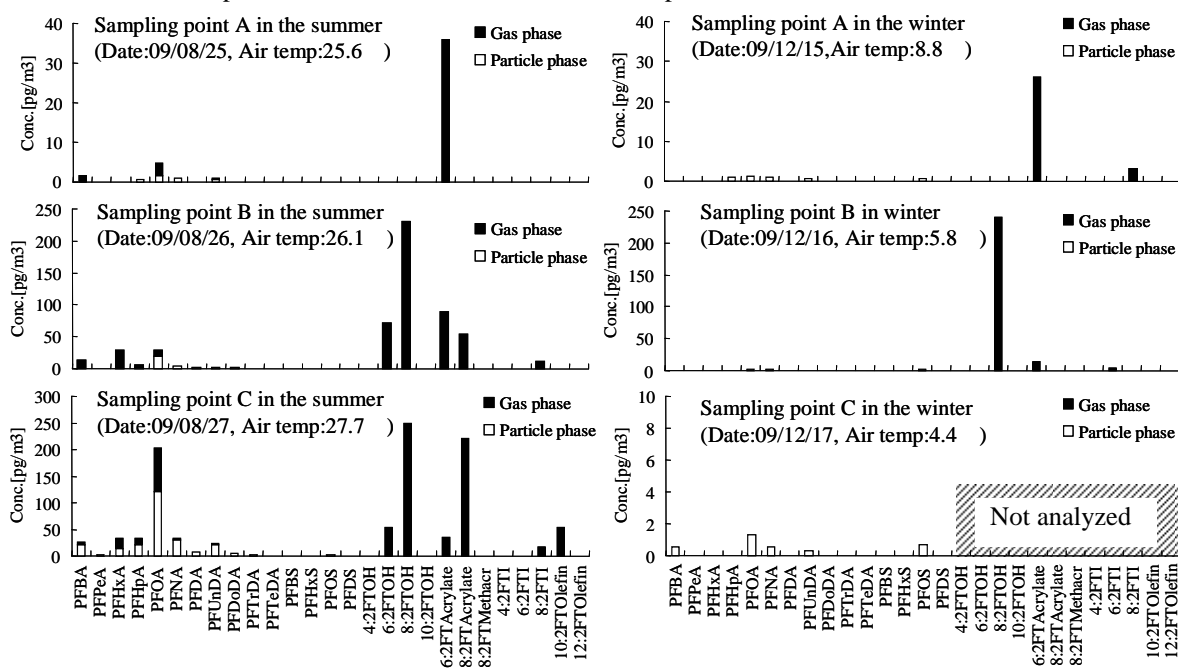


Fig.1 Gas phase and Particle phase distribution of PFCs from atmospheric samples collected on the sampling sites. Air temperatures were used AMeDAS (Automated Meteorological Data Acquisition System) data in neighboring the sampling points.

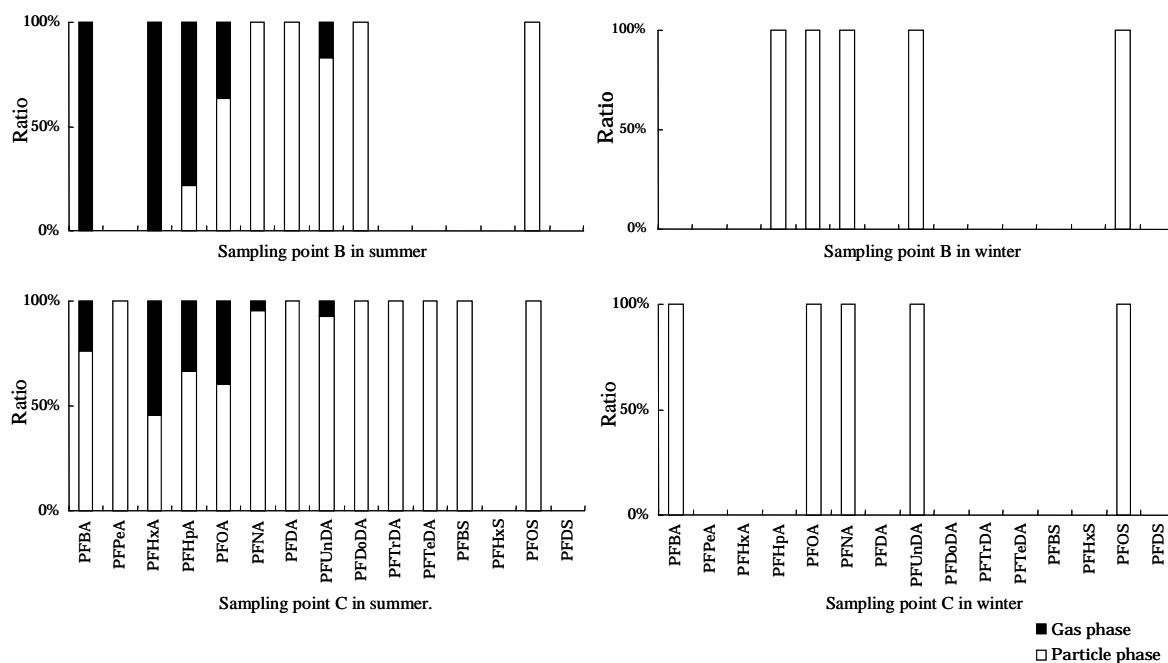


Fig.2 Gas/particle ratio of PFCAs and PFASs.

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