

ANNUAL DEPOSITION FLUX OF PFAS/PFCAS IN ATMOSPHERIC (DRY AND WET) DEPOSITIONS IN THE REGION OF OSAKA CITY, JAPAN

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Introduction

Perfluoroalkylsulfonates (PFASs) and perfluorocarboxylic acids (PFCAs) including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been identified in the environment. In particular PFOS have been found to be persistent, bioaccumulative and entailing toxic properties¹⁻⁵.

At its fourth meeting held May 2009, the Conference of the Parties (COP) of the Stockholm Convention decided to amend Annex B (restriction) to list it as POPs⁶. In addition, PFOA was also found in human blood in the general population, and has been aimed at EPA's "2010/15 PFOA Stewardship Program"⁷. In this way, the reduction of these substances has begun by international efforts. However, only limited data are currently available on PFASs/PFCAs including PFOS/PFOA⁸ for the atmospheric environment.

Because of the existence forms of PFASs/PFCAs in atmospheric (dry and wet) depositions are closely linked with those of the ambient air, it can be presumed that concentrations of PFASs/PFCAs in depositions are strongly correlated with those of the ambient air. Sampling of depositions is relatively easier than that of ambient air, it is suitable to understand the long-term variation of PFASs/PFCAs concentrations in atmosphere. Moreover, we can consider that measurement of PFASs/PFCAs in depositions is important for evaluation of transitions from atmospheric environment to other environmental phase such as soils, river water and sediment.

In this study, we examined to establish a highly selective and sensitive analytical method for PFASs/PFCAs in atmospheric (dry and wet) depositions and to calculate annual deposition flux of PFASs/PFCAs in depositions in the region of Osaka city, Japan.

Material and Methods

Annual deposition samples were collected using the measuring instrument for depositions (Dust Fall Sampler (Sibata Scientific Technology Ltd.)) according to deposit gauge method⁹ in every month from October 2010 to November 2011 at Osaka City Institute of Public Health and Environmental Sciences in Osaka City, Japan. After sampling, the solid phase (particle) and liquid phase (dissolved) are separated by filtration using a glass fiber filter (GFF; GC-50 (ADVANTEC)). Particle samples were spiked with 2 ng of two isotope-labelled C_{6,8}PFASs and seven isotope-labelled C_{4,6,8-12}PFCAs(MPFAC-MXA(Wellington Laboratories Inc.)) on GFF after drying.

Then, these samples were extracted from GFFs by ultrasonic extraction (15 min×3) with aqueous solution containing 10 % methanol (100 mL) as the extraction solvent. After the extraction step, the extracts were passed through a membrane filter and solid phase cartridge (OASIS WAX : Waters) for clean-up. The cartridges were eluted with 4 mL of 28 % ammonia solution/methanol (1/999). The eluate was spiked with injection standard (¹³C₈PFOS(Wellington) and ¹³C₈PFOA (CIL)) before that was concentrated under nitrogen gas flow to a final volume (1mL) for instrumental analysis. PFASs/PFCAs including PFOS/PFOA were analyzed by LC / (-) ESI-MS/MS (Xevo TQ MS:Waters), and recoveries of nine isotope-labelled PFASs/PFCAs were calculated respectively.

Dissolved samples were also spiked with 2 ng of two isotope-labelled C_{6,8}PFASs and seven isotope-labelled C_{4,6,8-12}PFCAs(MPFAC-MXA(Wellington Laboratories Inc.)). Samples were passed through a membrane filter and solid phase cartridge (OASIS WAX:Waters) for extraction and clean-up. Subsequent steps were also performed that of particle samples.

Dry deposition (Particle)

Wet deposition (Rain water)

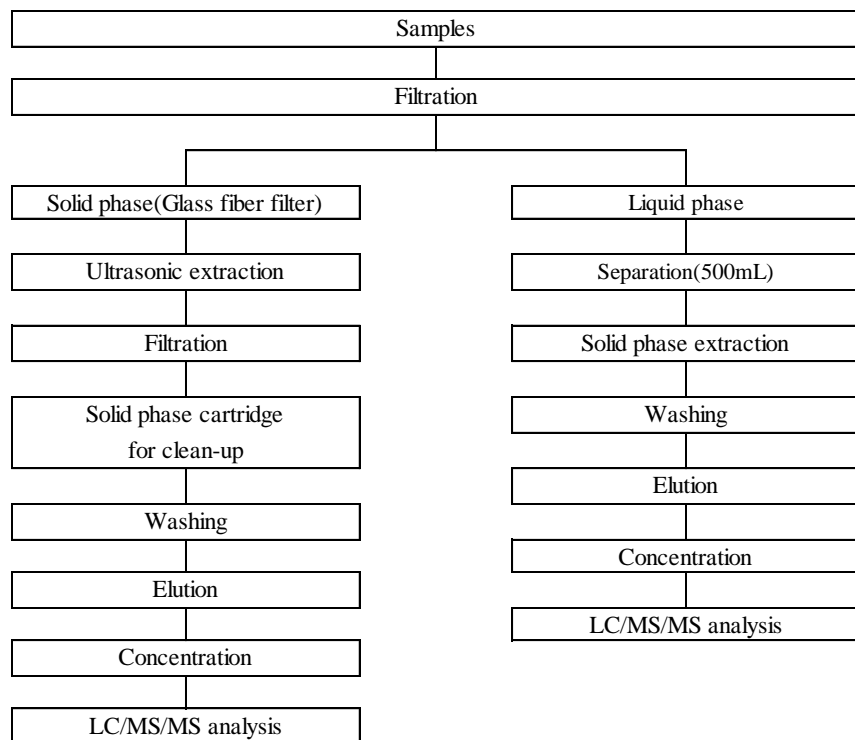


Fig.1 Summary of analytical methods for PFASs/PFCAs in dry and wet depositions

Results and Discussion

13 congeners of perfluoroalkylsulfonates (PFASs) and 4 congeners of perfluorocarboxylicacids (PFCAs) were targeted at this study (Table 1). In this study, the analyses of solid phase (particle) samples and liquid phase (dissolved) samples were carried out separately. The recovery efficiencies of the nine isotope-labelled PFASs/PFCAs (MPFBA, MPFHxA, MPFOA, MPFNA, MPFDA, MPFUdA, MPFDoA, MPFHxS and MPFOS) in particle(n=12) and dissolved(n=11) samples ranged from 42 to 130 % and from 44 to 160 %, respectively.

The concentrations of PFASs/PFCAs in particle samples were detected much lower than those of dissolved samples (the annual mean concentrations in particle and dissolved samples were 1.2 and 210 ng/m²/day, respectively). PFASs/PFCAs which were adsorbed particles might passed into liquid phase (dissolved) within the sampler because of these compounds have high aqueous property (for short-carbon chain compounds in particular). Therefore, PFASs/PFCAs in depositions were evaluated without separating particle and dissolved samples in this study.

The results of this study are shown in Table 2. The total concentrations

Table1 Target Compounds

PFASs	PFCAs
PFBS	PFBA
PFHxS	PFPeA
PFOS	PFHxA
PFDS	PFHpA
	PFOA
	PFNA
	PFDA
	PFUdA
	PFDoDA
	PFTtDA
	PFTeDA
	PFHxDA
	PFODA

of PFASs/PFCAs (the sum of 17 congeners; Table1) in atmospheric depositions were in a wide range (mean) of 0.48 to 990 ng/m²/day (190 ng/m²/day). Those of PFOS and PFOA were in a wide range (mean) of N.D. (<0.014) to 1.4 ng/m²/day (0.40 ng/m²/day) and N.D. (<0.59) to 290 ng/m²/day (53 ng/m²/day), respectively. PFASs/PFCAs, PFOS and PFOA concentrations in January 2011 showed much lower than other months. As it didn't rain throughout this month, dissolved sample could not be collected.

This result indicated that a large amount of PFASs/PFCAs in atmospheric environment was washed out by wet depositions (rain) compared with dry depositions.

Table2 Concentrations(ng/m²/day) of PFOS, PFOA and PFASs/PFCAs in atmospheric depositions in Osaka city, Japan

	Oct-10	Nov-10	Dec-10	Jan-11	Feb-11	Mar-11	Apr-11	May-11	Jun-11	Jul-11	Aug-11	Sep-11
PFOS	1.4	0.026	0.27	<0.014	0.30	0.24	0.18	0.24	0.24	0.35	1.0	0.51
PFOA	240	14	290	<0.59	15	6.2	3.1	6.8	17	13	22	14
PFASs	1.8	0.94	1.2	-	1.2	0.46	0.50	0.62	0.53	0.47	1.2	0.63
PFCAs	990	120	430	0.48	120	55	44	47	130	88	170	100
PFASs/PFCAs	990	120	430	0.48	120	55	44	47	130	91	170	100

PFASs/PFCAs concentrations at the four seasons were in a wide range (mean) of 100 to 990 ng/m²/day (400 ng/m²/day) for autumn (Sep.~Nov.), 0.48 to 430 ng/m²/day (180 ng/m²/day) for winter (Dec.~Feb.), 44 to 55 ng/m²/day (49 ng/m²/day) for spring (Mar.~May) and 91 to 170 ng/m²/day (130 ng/m²/day) for summer (Jun.~Aug.), respectively. The variation (about 10 times ; except Jan.) of PFASs/PFCAs concentrations among each month in the same season was largely compared to the difference (about 8 times) of mean concentrations between autumn and spring. It was indicated that the change of concentration is not correlated with the temperature. Moreover, it was not found either that the other meteorological conditions such as precipitation and amount of particles relate to amount of PFASs/PFCAs depositions. These results suggest that it is necessary to understand the emission amount of PFASs/PFCAs from their sources located around sampling site.

It is important to understand the movement of PFASs/PFCAs from their sources, through the atmosphere, to their sink such as soil or sediment. Therefore, we examined to calculate annual deposition flux of PFASs/PFCAs in atmospheric depositions in the region of Osaka city, Japan. The relationship between the annual deposition flux and concentrations can be derived from the equation.

Annual deposition flux (ng) = Concentration of depositions (ng/m²/day) × Area (m²) × Number of days (day)
 where “concentration of depositions” are mean concentrations of PFASs/PFCAs, PFOS, PFOA in this study (190, 0.40, 53 ng/m²/day), respectively ; “Area” is total area of Osaka city, Japan (222.47 km² as reported by Geographical Survey Institute, Japan) and “Number of days” is 365 days. The annual deposition flux of PFASs/PFCAs, PFOS, PFOA in Osaka city area were calculated 15, 0.032, 4.3 kg/(m² yr), respectively.

Acknowledgements

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