

Cod: 4.4006

SIZE SPECIFIC DISTRIBUTION ANALYSIS FOR PERFLUORO ALKYL SUBSTANCES IN ATMOSPHERIC PARTICULATE MATTERS – SAMPLING METHOD DEVELOPMENT AND INDOOR/AMBIENT AIR CONCENTRATION

H. Ge¹, E. Yamazaki², N. Yamashita², S. Taniyasu², T. Zhang³, M. Hata³, M. Furuuchi³

¹National Institute of Advanced Industrial Science and Technology; Kanazawa University

²National Institute of Advanced Industrial Science and Technology

³Kanazawa University

Introduction

The international regulation of persistent organic pollutants (POPs) according to the Stockholm convention started in May 2001, to regulate production and use of hazardous chemicals in global scale. PFOS was one of newly listed as emerging POPs and only one of huge group of perfluoroalkyl substances (PFASs), it was known as “super set” of chemical tracers including more than ninety related chemicals. Previous research indicates that PFASs, due to their persistence, water solubility, and measurability, could represent excellent tracers of global circulation of oceanic waters¹. Comprehensive monitoring of PFASs is necessary to make reliable understanding of environmental kinetics. However, atmospheric pollution by PFASs is still unclear because their existence condition was not fully understood yet. Hence, reliable analytical method to measure exact residue of PFASs in air particles is needed. In this study, in order to investigate PFASs in atmospheric particles including PM_{2.5}, performance of new sampling equipment was testified by sampling in a stable indoor environment multiple times. Meanwhile, by sampling simultaneously at a roadside environment, PFASs characters in two different types of air environment have been compared.

Material and Methods

Air sampling conducted in two locations representing two typical air environment. One is an isolated meeting room with controlled temperature (25°C) and relative humidity (45±10%), which representing enclosed indoor environment. The other is ambient air from a campus of the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, 10 meters away from a busy traffic road, which representing roadside environment. Two Nanosampers², operated at 40L/min, were used during these air sampling. The inlet and filter stages allowed collection of particles in five size fractions including particle diameter (dp) greater than 10µm and less than 0.5µm (specifically, >10, 10–2.5, 2.5–1, 1–0.5, and < 0.5 µm, respectively). These air experiments were conducted both summer and winter time, total ten sets of indoor samples and ten sets of Roadside samples have been collected. Table 1 shows the detail air sampling information.

In order to investigate PFASs recovery rate after air sampling and sample extraction, filters on the first stage of sampler were spiked with 1 pg of ¹³C-labeled internal standards prior to air sampling (¹³C₂-PFBA, ¹³C₄-PFOA, ¹³C₅-PFNA, ¹³C₂-PFDA and ¹³C₄-PFOS).

Ambient particles were collected on quartz fiber filters (QFF, Pallflex, 2500QAT-UP). QFF were pre-baked at 350 °C for 3 hours to remove possible contamination. All filters were conditioned in a weighing chamber with a controlled temperature (21±1°C) and relative humidity (35±2% RH) for 48 hours and the weight was measured using a microbalance (readability to 1 µg) before and after the sampling.

For chemical analysis, filters have been put into a PP tube and sonic extracted (10min, 40°C) with methanol (4mL*3 times). The supernatant was collected in a new PP tube, concentrated to 1mL under a nitrogen stream and transferred into a vial for analysis.

The HPLC tandem mass spectrometry (HPLC-MS/MS) was used for measure concentration of target compounds. Total 23 kinds of PFASs (Seven perfluoro sulfonic acids (PFSAs), fifteen perfluoro carboxylic acids (PFCAs), FOSA, N-EtFOSA, N-EtFOSAA, and 8:2FTOH) were analyzed^{3,4}.

Laboratory blanks and recoveries were analyzed with each set of samples as a check for possible laboratory contamination and interferences. Blanks did not contain any interference. Recoveries of these 23 kinds of PFASs had been spiked onto quartz fiber filters and treated using analytical procedures. Reported PFASs concentrations were not corrected for recovery.

Results and discussion

The following results were observed from overview of sampling using nanosampler. The indoor air profile was dominated by FOSA(5.7 pg/m³), N-EtFOSAA(4.7 pg/m³), PFNA(4.1 pg/m³) and N-EtFOSA(3.0 pg/m³), while the roadside air profile was dominated by PFHxA(7.3 pg/m³), PFHpA(3.7 pg/m³), PFOA(3.1 pg/m³) and PFNA(2.6 pg/m³). Greater variations have been observed for individual PFASs in roadside air particles, which may due to temporal variation from summer to winter. The concentrations of three volatile PFASs (FOSA, N-EtFOSA, N-EtFOSAA) in Indoor particles exceed substantially those of Roadside particles. The Indoor/ Roadside ratios of these three compounds were 10.3, 10.8, 5.3, respectably. Meanwhile, the concentration of carboxylate (C4-C8) in roadside particles were increased comparing with those of Indoor particles. The Indoor/ Roadside ratios of these compounds varied from 0.26 (PFHpA) to 0.76 (PFOA). This result suggest that other than indoor emissions are driving outdoor contamination⁵, for the roadside environment, there seem to exists other contamination source that is responsible for concentrations of carboxylate PFASs in particles. Also, in the roadside air, average concentration of PFHxA exceeded that of PFOA, which is consistent with the hypothesis that PFHxA use is increasing in response to restrictions on the use of PFOA.

Fig.1 shows the percentage of average concentrations fine particle (particle size smaller than 2.5 μ m): coarse particle (particle size larger than 2.5 μ m) for PFASs. In indoor air, each individual PFASs concentrations in fine particles contributed over 50% in all particles with the exception of PFBS and PFBA, while in roadside environment, 11 out of 20 PFASs concentrations in fine particles contributed over 50% in all particles. Furthermore, in roadside air, for C4-C10 PFCA, the attribution of PM_{2.5} was increasing along with carbon chain length.

To our knowledge, this is the first report about individual PFASs measurement in size segregated particulate samples from the environment. Present result and developed sampling method in this study enable more accurate understanding of kinetics of individual PFASs in the environment.

References:

1. Yamashita, N., Taniyasu, S., Petrick, G., Wei, S., Gamo, T., Lam, P. K., & Kannan, K. (2008). *Chemosphere*, 70(7), 1247-1255.
2. Furuuchi, M., Eryu, K., Nagura, M., Hata, M., Kato, T., Tajima, N., ... & Otani, Y. (2010). *Aerosol Air Qual. Res*, 10, 185-192.
3. Taniyasu, S., Kannan, K., So, M. K., Gulkowska, A., Sinclair, E., Okazawa, T., & Yamashita, N. (2005). *Journal of Chromatography A*, 1093(1), 89-97.
4. Taniyasu, S., Kannan, K., Yeung, L. W., Kwok, K. Y., Lam, P. K., & Yamashita, N. (2008). *Analytica Chimica Acta*, 619(2), 221-230.
5. Goosey E, Harrad S. *Environment international*, 2012, 45: 86-90.

Table 1 Air sampling information

		Location	Sampling time			Spiked standard
			Start date	End date	Total time(h)	
Indoor	MR1	Meeting Room	14/09/26	14/09/28	44	surrogate
	MR2	Meeting Room	14/10/16	14/10/19	66.4	surrogate
	MR3	Meeting Room	15/07/17	15/07/19	40	surrogate
	MR4	Meeting Room	15/07/17	15/07/19	40	surrogate
	MR5	Meeting Room	15/07/19	15/07/21	42.4	surrogate
	MR6	Meeting Room	15/07/19	15/07/21	42.4	surrogate
	MR7	Meeting Room	15/08/07	15/08/10	63.9	surrogate
	MR8	Meeting Room	15/08/07	15/08/10	63.9	surrogate
	MR9	Meeting Room	16/02/19	16/02/22	65.2	surrogate
	MR10	Meeting Room	16/02/19	16/02/22	65.2	surrogate
Roadside	RS1	AIST Main gate	15/07/21	15/07/22	24.8	surrogate
	RS2	AIST Main gate	15/07/21	15/07/22	24.8	surrogate
	RS3	AIST Main gate	15/08/06	15/08/07	27.6	surrogate
	RS4	AIST Main gate	15/08/06	15/08/07	27.6	surrogate
	RS5	AIST Main gate	15/08/10	15/08/11	27.8	surrogate
	RS6	AIST Main gate	15/08/10	15/08/11	27.8	surrogate
	RS7	AIST Main gate	16/02/18	16/02/19	25.6	surrogate
	RS8	AIST Main gate	16/02/18	16/02/19	25.6	surrogate
	RS9	AIST Main gate	16/02/22	16/02/24	45.8	surrogate
	RS10	AIST Main gate	16/02/22	16/02/24	45.8	surrogate

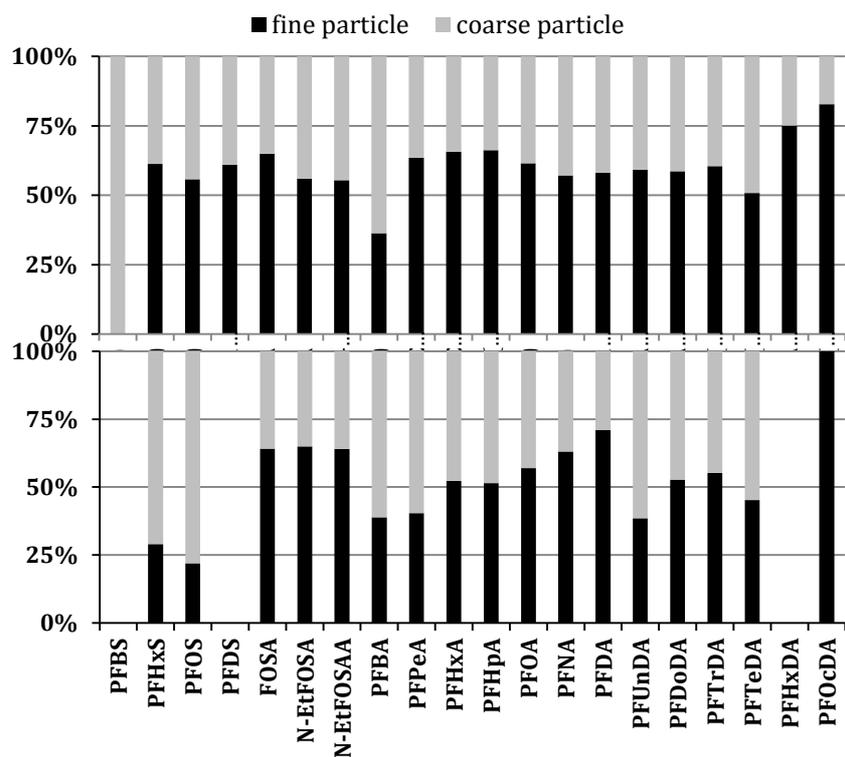


Figure 1 Percentage of average concentrations fine particle: coarse particle for PFASs