

PERFLUORO ALKYL SUBSTANCES IN ATMOSPHERIC PARTICULATE MATTERS – SIZE SPECIFIC DISTRIBUTION ANALYSIS

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Introduction

Starting from May 2001, to regulate the production and use of hazardous chemicals at the global scale, and protect nature from inconsiderate discharges of chemicals, a total of 164 countries and the European Union made agreement conclude with this rule. Considering the recent situation of worldwide use of new hazardous chemicals, the previous list was updated and new chemicals were added recently. PFOS (PFOSF) is one of the chemicals newly listed as an emerging POP and as the only member of the large group of perfluoroalkyl substances (PFASs), it was known as “super set” of chemical tracers including more than 90 related chemicals. Previous research indicates that PFAs, 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 enable reliable understanding of environmental kinetics. However, atmospheric pollution by PFASs is still unclear because their existence condition is not fully understood yet. Although particulate PFASs, such as PFOS could be partitioned in aerosol and smaller particles in air, huge amount of volatile PFASs and possible precursors are supposed to remain in the gas phase. Hence, reliable analytical method to measure the exact residue of PFASs in particles is needed. In this study, new sampling equipment was developed to investigate PFASs in atmospheric particles including PM_{2.5} tested in general atmosphere.

Materials and methods

As a preliminary work to investigate atmospheric pollution of PFASs, three experiments were carried out. The first one is to elucidate possible contamination of target chemicals during sampling procedure since widely used fluoro-polymers in sampling apparatus could be source of contamination. In this experiment, each small parts of NS sampler parts has been washed twice by 10ml MeOH, condensed to 1ml separately and analyzed. The second one is to establish QA/QC system for particle sampling and chemical analysis. Nanosampler (NS40, Fig. 1), operated at 40L/min, was used for size selective collection of particle in atmosphere. The inlet and filter stages allowed collection of particles in six size fractions including particle diameter (dp) greater than 10µm and less than 0.1µm (specifically, >10, 10–2.5, 2.5–1, 1–0.5, 0.5–0.1, and < 0.1 µm, respectively). ¹³C PFASs was spiked on the first stage filter of NS40 and kept sampling for 48 hrs in an stable indoor environment (25±2 °C, 40±10%RH). After sampling, all filters have been analyzed to check recovery rate of chemicals. Another experiment is to investigate size dependent partitioning of each chemical in aerosol. Samples were collected in several locations of Japan, Hong Kong and India.

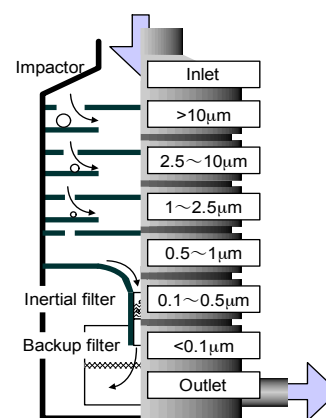


Fig 1 diagram of NS40

Mainly two procedures were conducted in these experiments. One is filter weighing. Ambient particles were collected on quartz fiber filters (QFF, Pallflex, 2500QAT-UP) except 0.1-0.5µm stage, which use inertial filter cartridge along with stainless steel fiber². QFF were pre-baked at 350 °C for 2 hours to remove possible contamination. All filters were conditioned at 21.5°C and 35% RH in a weighing chamber (Tokyo dyrec PWS-PM2.5) for 48 hours and measured weight using a Sartorius M5-F microbalance (readability to 1 µg) before and after the sampling.

The other is filter extraction. Particle samples collected were extracted using methanol and measured by HPLC-tandem mass spectrometry. Seven perfluoro sulfonic acids (PFSA), fifteen perfluoro carboxylic acids (PFCAs), PFOSA, N-EtFOSA, N-EtFOSAA, N-MeFOSE, N-EtFOSE, 8:2FTCA, 6:2, 8:2, 10:2FTUCA, 4:2FTOH, 6:2FTOH, and 8:2FTOH were analyzed^{3,4}.

Results and discussion

Blank check

One remarkable finding of this study is the identification of blank contamination in the plastic and rubber materials used as parts of the particle sampler. This makes it clear that commercially available particle matter samplers with many parts made with fluoro polymer/rubber materials are not suitable in measuring PFASs in the atmosphere. We tested every small part of the sampler to remove possible contamination with PFASs and successfully developed blank-free particle sampler for PFASs analyses.

Quality assurance / quality control (QA/QC) establishment

NS recovery test repeated twice in 1st meeting room, main building, AIST. Result shows 13C PFASs recovery rates of first stage QFF are between 87-113% (Fig.2), while recovery rates of other stages filters is below 3%. This result indicates most PFASs would remain on collected filters and no obvious chemical re-suspension occurred along with sampling flow rate. QA/QC system ensured reliable experiment procedure and high recovery rate for PFASs.

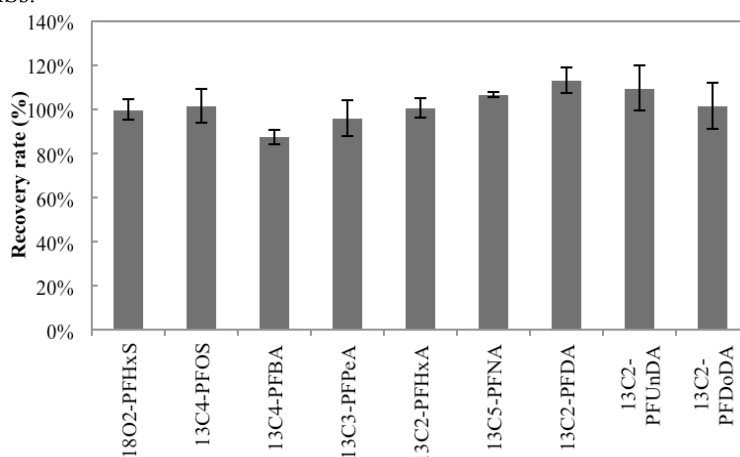


Fig 2 recovery rates of ¹³C PFASs, error bar represents standard deviations .

Field sample analyzing

Field particle samples were collected using NS in several places of Japan (Kanazawa, Okinawa), Hong Kong and India. Kanazawa monitoring site is located in campus of Kanazawa University, a mountainous area without notable emission sources. Okinawa monitoring site is located in a peaceful residential area, 3km from seashore. Kowloon sampling site is on one building rooftop of City University of Hong Kong, surrounded by high population density residential area combined with heavy traffic. Chennai sampling site is in Madras University campus, only 1km from seashore. Furthermore, for studying ocean aerosol, on board sampling was carried out during open ocean surveys using "Hakuho-maru" research vessel (KH14-06, from Japan to Antarctic Sea).

(a) Mass concentration and size distribution

PM₁₀, PM_{2.5} concentration information is listed in Table 1. The highest mass concentration was witnessed at Hong Kong (October 2014), followed by Chennai, Hong Kong (July 2014) and two places in Japan. The size distribution, cumulative under mass fraction of collected air samples is showed in Fig.3. High similarity was observed for Okinawa and Chennai samples. These samples all contain relatively high portions of coarse particles ($2.5\mu\text{m} < dp < 10\mu\text{m}$) which may have been caused by sea salt.

(b) PFASs concentration

Fig.4 shows size segregated PFASs concentrations in the atmosphere with PFOS, PFBA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFTrDA, PFTeDA and PFHxDA. Each compounds' concentration are shown according to six aerosol size fractions (specifically, >10 , $10-2.5$, $2.5-1$, $1-0.5$, $0.5-0.1$, and $< 0.1 \mu\text{m}$, respectively). In general, relatively high PFOA concentrations were detected, followed by PFNA, PFDA and PFHpA.

Table 1 Sampling information and PM concentration

Location		Flow rate (L/min)	Sampling time			Total volume (m ³)	PM concentration	
City /Country	detail		start date	end date	Total time(h)		PM ₁₀	PM _{2.5}
Kanazawa, Japan	Kanazawa Univ., 6F(balcony)	40	14/04/16	14/04/23	167.5	402.0	28.4	20.7
		40	14/04/23	14/04/30	167.2	401.2	17.9	14.2
Okinawa, Japan	Residential area of Ginowan city	40	14/04/05	14/04/12	170.0	408.0	26.8	15.4
		40	14/04/13	13/04/20	170.0	408.0	24.6	11.9
Kowloon, HongKong	City Univ., rooftop	40	14/07/06	14/07/10	95.4	229.0	43.8	31.8
		40	14/07/10	14/07/13	70.5	169.2	30.1	18.9
		40	14/10/28	14/10/29	26.5	63.5	112.2	71.8
		40	14/10/29	14/10/31	39.7	95.3	71.3	42.5
Chennai, India	Madras Univ., 3F	40	14/05/25	14/05/27	48.0	115.2	68.3	31.8
		39.5	14/05/27	14/05/29	48.0	113.8	63.0	36.6
Southern Pacific Ocean	S50, W170 to S36, E170.5	38	15/01/09	15/01/18	133.1	303.5	11.3	6.0
Northeastern Pacific Ocean	N7, E171 to N12.6, E144	38	15/02/14	15/02/18	88.0	200.6	20.2	10.4

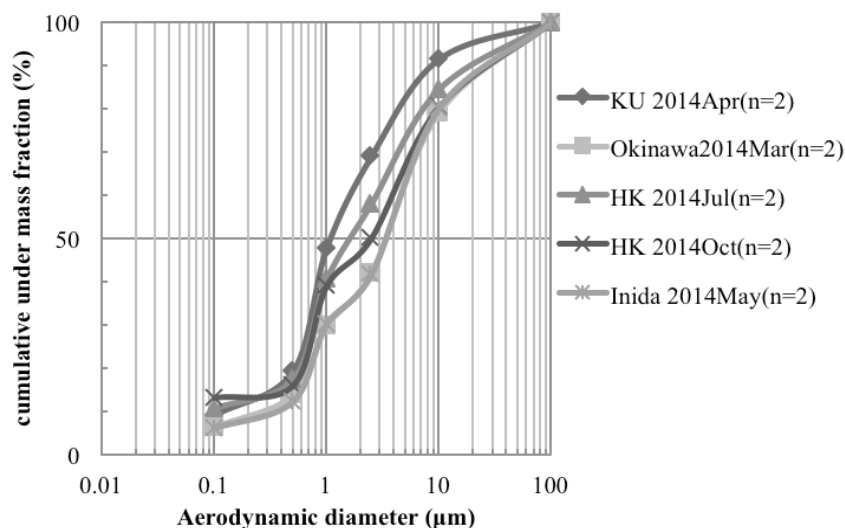


Fig 3 cumulative under mass fraction of collected air samples (%)

Size dependent accumulations revealed reasonable understanding of the partitioning of each chemical according to their physicochemical properties. Possible breakthrough of volatile PFASs was evaluated using newly developed cryogenic moisture sampler (CMS)⁵

Acknowledgements

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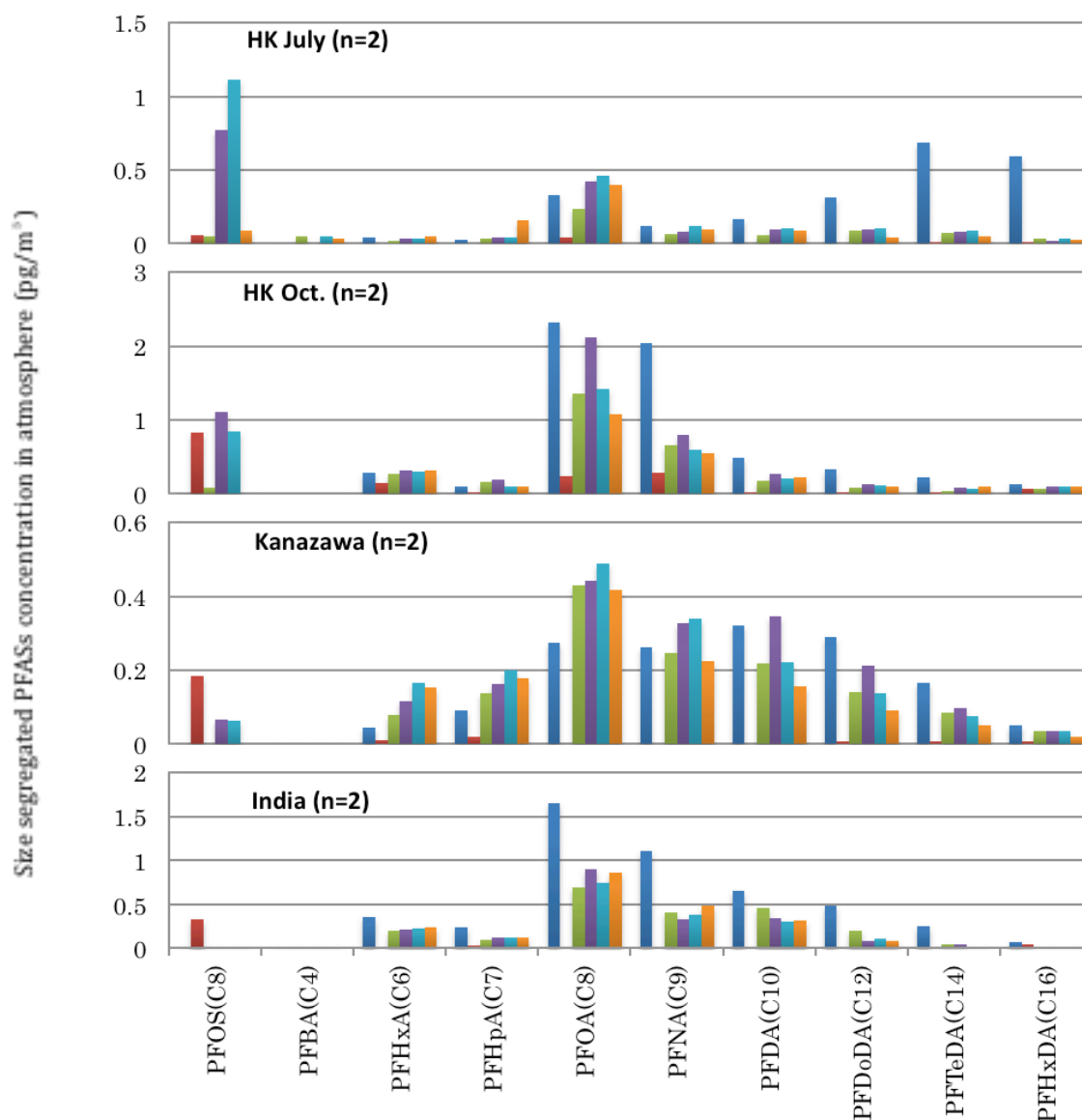


Fig 4 Size segregated PFASs concentration in atmosphere (pg/m³)