

Atmospheric Concentrations of Particle and Gas Phase Per- and Polyfluoroalkyl Substances (PFAS) in Osaka, Japan

Daichi Asakawa^{1*}, Toshiki Tojo¹, Makiko Ichihara¹, Sachi Taniyasu², Nobuyasu Hanari³, Nobuyoshi Yamashita²

¹ Osaka City Research Center of Environmental Science, 8-34 Tojo, Tennoji-ku, Osaka, 543-0026, Japan, d-asakawa@city.osaka.lg.jp, daichi.asakawa@gmail.com

² National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki, 305-8569, Japan

³ National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology (NMIJ/AIST) 1-1-1, Umezono, Tsukuba, Ibaraki, Japan

1 Introduction

Per- and polyfluoroalkyl substances (PFASs) are aliphatic substances containing one or more perfluoroalkyl moieties that have high surface activity and stability. Due to their unique physicochemical properties, PFASs have been widely used in industrial and commercial products, such as surfactants, cosmetics, and food contact materials. Unfortunately, its chemical and thermal stability have resulted in global pollution. Concentrations and distribution of PFASs in humans and wildlife have been reported in many publications [e.g., 1]. A significant correlation between the concentration of perfluorooctane sulfonate (PFOS) and the age of polar bears [1] indicates bioaccumulation of PFASs. Adverse health effects of PFASs, including altered immune and thyroid function, liver disease, kidney disease, and cancer, have also been revealed in epidemiological studies [2]. Therefore, PFASs are now a major global problem of environmental pollution and the elimination of PFASs emissions is an urgent issue.

The Stockholm Convention on Persistent Organic Pollutants (POPs) has listed perfluorooctanoic acid (PFOA), PFOS, and perfluorohexane sulfonic acid (PFHxS) as compounds that should be eliminated or restricted in their production and use. More recently, POPs Review Committee (POPRC) is also considering listing long-chain perfluorocarboxylic acids (C₉–C₂₁ PFCAs). To manage and evaluate the risks of these PFASs and related compounds including precursors, risk profiling based on environmental monitoring data is essentially important. In Japan, PFOA and PFOS in air, water, sediment, and wildlife have been monitored by the Ministry of the Environment since 2010 [3]. This monitoring project has used the high-volume (HV) air sampler equipped with a quartz filter followed by polyurethane foam (PUF) and an activated charcoal filter. For a more comprehensive understanding of the environmental pollution of PFASs, our group developed a novel atmospheric PFASs sampler and an activated charcoal fiber (GAIACTM). The new air sampling technique enabled us to quantify more than 40 ionic and neutral PFASs in particle and gas phases and had applied to air sampling in suburban areas in Japan [4], indoor and outdoor air [5], and open ocean [6]. In this study, the developed sampler (FM4) was used to measure ionic PFASs (including some neutral PFASs) in the air in Japan, and the results were compared and validated with those measured by the conventional HV sampler.

2 Materials and Methods

2.1 Reagents and Materials

Native and labeled stock solutions of PFASs mixtures for ISO 21675 were purchased from Wellington laboratories (Guelph, Ontario, Canada). Native PFASs mixture contained 13 PFCAs (C₄–C₁₄, C₁₆, C₁₈: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDODA, PFTrDA, PFTeDA, PFHxDA, PFOcDA), 5 perfluoroalkyl sulfonic acids (C₄, C₆–C₉ PFASs: PFBS, PFHxS, PFHpS, PFOS, PFDS), 3 perfluorooctane sulfonamides (FOSAs: FOSA, N-MeFOSA, N-EtFOSA), 2 perfluorooctane sulfonamidoacetic acids (FOSAAs: N-MeFOSAA, N-EtFOSAA), 2 fluorotelomer sulfonic acids (FTSAs: 6:2 FTSA, 8:2 FTSA), 8:2 fluorotelomer unsaturated carboxylic acid (8:2 FTUCA), and 4 other PFASs (9Cl-PF₃ONS, 8:2 diPAP, HFPO-DA, DONA). The labeled PFAS mixture and ¹³C₄-PFOS (Wellington laboratories) were used as surrogate and syringe spikes, respectively. Extraction solvent (special grade methanol, ethyl acetate, dichloromethane, acetone, and toluene) and mobile phase for liquid chromatography (LC-MS/MS grade methanol) were obtained from Kanto Chemical (Tokyo, Japan). We used water purified by PURELAB flex3 (ELGA LabWater, Lane End, UK) and ensured that PFAS contamination levels of the water were sufficiently low before use. OasisTM WAX solid phase extraction (SPE) cartridge (150 mg, 30 μm) was purchased from Waters (Milford, MA, USA). HPLC grade ammonia solution (25%) and ammonium acetate solution (1 mol/L) were supplied by Merck (Darmstadt, Germany) and Nacalai Tesque (Kyoto, Japan), respectively. Quartz fiber filter (QFF; 31- and 47-mm dia.; Pall, New York, USA), PUF (47 mm dia., 50 mm thick; Sibata Scientific Technology, Tokyo, Japan), and GAIACTM (47 mm dia., 2 mm thick; Futamura Chemical, Gifu, Japan) were used for air sampling media. Prior to sampling, QFF was prebaked at 350°C for 3h, and PUF and GAIACTM were cleaned up with water, methanol, ethyl acetate, and dichloromethane, successively. For HV sampling, a square quartz fiber filter

(8×10 inch) was purchased from ADVANTEC (Tokyo, Japan) and PUF (90 mm dia., 50 mm thick) and activated charcoal fiber filter (ACFF; 84 mm dia.) were from Sibata Scientific Technology (Tokyo, Japan). The PUF and ACF for HV sampling were pre-cleaned by Soxhlet extraction using acetone and toluene.

2.2 Air sampling

Atmospheric PFASs were collected using an FM4 air sampler (GL Science, Tokyo, Japan) that is comprised of a four-stage cascade impactor followed by a PUF and GAIAC™ holder (Figure 1). Size segregated particulate PFASs (>10 μm, 2.5–10 μm, 1.0–2.5 μm, <1.0 μm) were collected on QFFs, and gaseous PFASs were adsorbed on a PUF and two GAIAC™. Air sampling was conducted at a flow rate of 20 L/min for 48 h during warm and cold seasons in 2021/2022 at Osaka city which is a metropolis in west Japan. Meteorological conditions during sampling are shown in Table 1 in brief.

To compare the FM4 and HV sampling techniques, we also operated the FM4 and HV samplers concurrently during the warm season ($n=3$). A flow rate of the HV sampler equipped with square QFF, PUF, and ACFF was 100 L/min. The surrogate solution was added before sampling according to the manual of Environmental Survey and Monitoring of Chemicals by the Japan Ministry of the Environment [3].

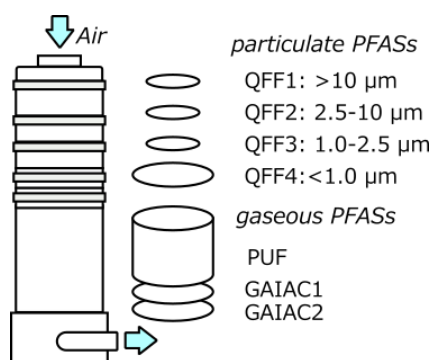


Figure 1: Illustration of FM4 air sampler.

Table 1: Meteorological conditions during sampling campaign.

Season	Date	Temp (°C)*	RH (%)	Press. (hPa)	Rainfall (mm)
Warm	2021/9/4–6	22.1–30.4 (25.7)	69	1005	0.5
	2021/10/5–7	20.2–29.7 (24.2)	65	1009	-
	2021/10/7–9	21.9–30.3 (25.6)	68	1011	-
Cold	2022/1/18–20	1.1–6.8 (4.3)	62	1009	-
	2022/1/20–22	1.3–8.4 (4.0)	58	1016	-
	2022/2/1–3	2.7–9.1 (6.5)	54	1011	-

*Minimum–maximum (mean)

2.3 Sample treatment

Extraction and concentration methods for FM4 sample were based on the previous report [5] with some modifications. Briefly, a surrogate solution was spiked to sampling media before extraction. QFF was extracted by ethyl acetate/dichloromethane (1:1, v/v) and methanol successively. Extractant for PUF and GAIAC™ were almost same to that for QFF, but 0.01 % ammonia was added to methanol. Both extracts were concentrated under gentle nitrogen stream and added a syringe spike solution and methanol. The methanol solutions were injected into the liquid chromatography-tandem mass spectrometer (LC-MS/MS) for measurement of the target PFASs.

Samples collected by HV sampler were extracted using Soxhlet apparatus with acetone. The extracts of QFF, PUF, and ACFF were combined and concentrated by evaporator. This fraction was acidified by addition of water and formic acid, and then passed through the SPE cartridge. The ionic PFASs retained on SPE cartridge were eluted by methanol containing 2% ammonia and concentrated under nitrogen stream. After the addition of the syringe spike to this fraction, this solution was applied to LC-MS/MS analysis. The sample that collected by FM4 for comparison with HV was extracted as described above, but extracts of QFF, PUF and GAIAC™ were combined because of distribution of sampling surrogates.

2.4 Instrumental analysis

LC-MS/MS analysis was conducted by an ExionLC liquid chromatograph coupled with a Triple Quad 4500 tandem mass spectrometer (AB Sciex, Foster City, CA, USA). Conditions of LC-MS/MS analysis were referred to ISO 21675 and briefly listed as follows: analytical column, Betasil C18 (2.1×50 mm, 5 μm; Thermo Scientific, Waltham, MA, USA); guard column, Eclipse XDB C8 (2.1×12.5 mm, 5 μm; Agilent Technologies, Santa Clara, CA, USA); retention gap column, delay column for PFAS (2.0×30 mm; GL Science, Tokyo, Japan); mobile phase, 2 mM ammonium acetate and methanol; column temperature, 30°C; injection volume, 5 μL; flow rate, 0.22 mL/min; ionization, ESI negative; acquisition mode, multiple reaction monitoring; source temperature, 450°C. Before injection, 5 μL of sample solution was mixed with 10 μL of 2 mM ammonium acetate using autosampler.

3 Results

3.1 Comparison with the new FM4 sampler and the conventional HV sampler

Ratios of measured concentrations of PFCAs and PFASs collected by the FM4 sampler to those by HV sampler are shown in Figure 2. Mean values of the ratio of PFCAs and PFASs were 0.67–1.2 and 0.55–0.92, respectively. The ratios of PFOA and PFOS that were target analytes of the conventional HV sampling method were 0.74 ± 0.46 and 0.85 ± 0.43 , respectively. The recoveries of surrogate PFCAs and PFASs of FM4 sampling method (53–120 %) were higher than those of HV sampling method (18–80 %), except for $^{13}\text{C}_4$ -PFHxA. The recoveries of $^{13}\text{C}_4$ -PFHxA of both methods were about 35%.

3.2 Atmospheric concentrations of PFASs in Osaka, Japan

The detection limits of the targeted PFASs in this study were 0.013–0.13 pg/m³. We detected 29 PFASs, namely 13 PFCAs, 5 PFASs, FOSA, N-MeFOSA, N-EtFOSA, N-MeFOSAA, N-EtFOSAA, 6:2 FTSA, 8:2 FTSA, 9Cl-PF₃ONS, 8:2 FTUCA, 8:2 diPAP, and HFPO-DA, from the samples collected in the warm and the cold seasons in Osaka, Japan. The sum of concentrations of particle and gas phase PFASs was 190–1,800 pg/m³ and the predominant PFASs were PFBA, PFHxA, PFOA, and PFBS. The total concentrations of PFCAs were 290–1,600 pg/m³ and 120–260 pg/m³ in the warm and the cold seasons, respectively. The total concentration of PFASs in the warm season (69–130 pg/m³) was similar to that in the cold season (67–130 pg/m³).

Figure 3 shows the particle size and phase distributions of the PFASs detected in this study. The concentrations and compositions of individual PFASs varied with samples. The concentrations of PFOA and PFOS, which have been monitored by the HV sampling method in Japan, were 7.3–210 pg/m³ and 1.2–5.6 pg/m³, respectively. The concentration of 6:2 FTSA ranged from below the detection limit to 46 pg/m³. The concentrations of other PFASs except for PFCAs and PFASs were less than 5 pg/m³.

As shown in Figure 3, the PFASs were mainly detected from the PUF and GAIACTM except for 6:2 FTSA, indicating that the PFASs were predominantly in the gas phase in our sample. Gas-particle partitioning of the PFASs was described using particle-associated fraction which was defined as a ratio of the PFAS concentration associated with the particle phase over the sum of gas and particle phases concentrations. The particle-associated fraction of short-chain PFCAs (PFBA; 0.009 ± 0.07) was lower than that of long-chain PFCAs (PFOA; 0.037 ± 0.020 , PFOcDA; 0.24 ± 0.10). Additionally, the particle-associated fractions of PFOS (0.028 ± 0.028) and 6:2 FTSA (0.99 ± 0.012) were suggested that these PFASs predominantly distributed in the gas phase and particle phase, respectively. The difference in the distribution between sampling seasons was found in HFPO-DA (also known as GenX). The particle-associated fraction of HFPO-DA in the warm season (0.072 ± 0.020) was relatively lower than that in the cold season (0.329 ± 0.010).

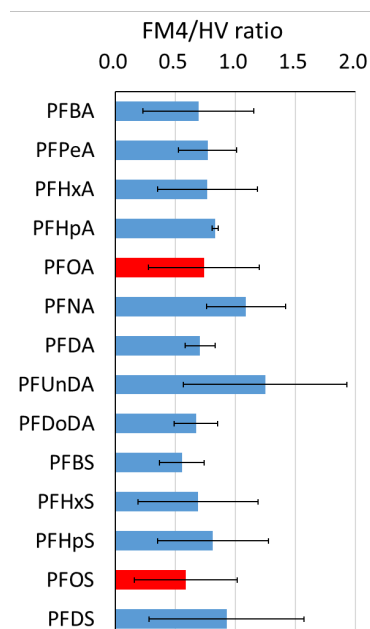


Figure 2: Ratios of concentrations of PFASs of FM4 sampling method to those of HV sampling method.

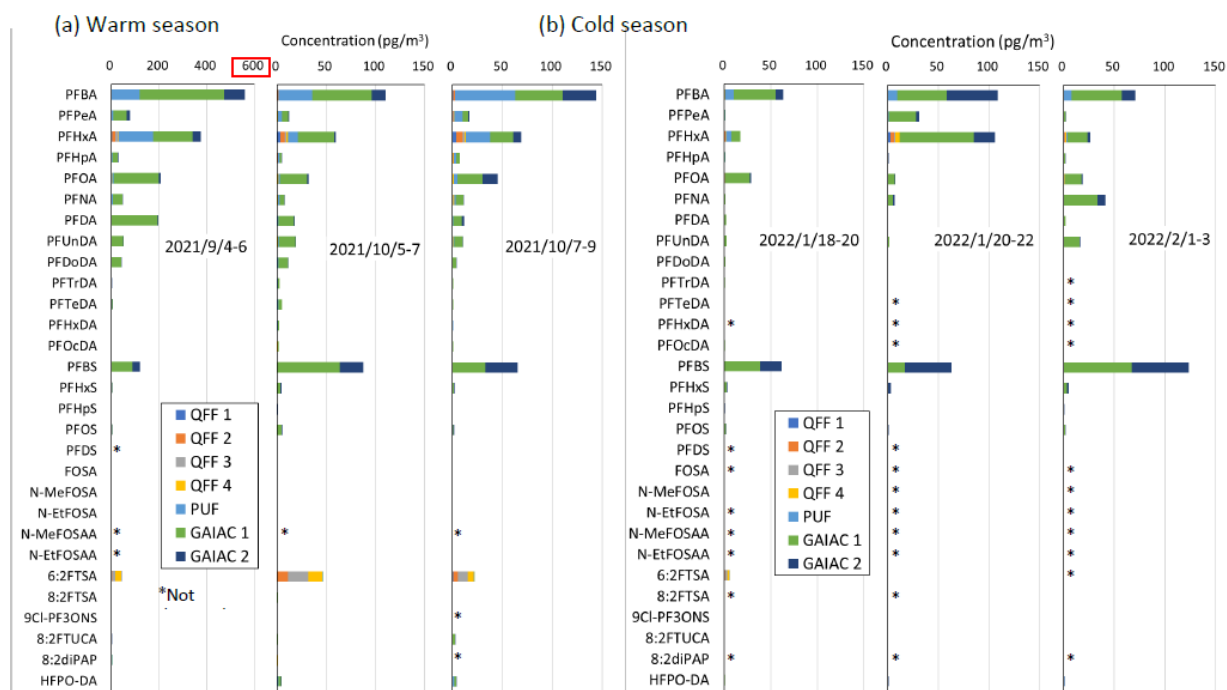


Figure 3: Particle size and phase distributions of the detected PFASs in the warm (a) and the cold seasons (b).

4 Discussion

4.1 Comparison with the new FM4 sampler and the conventional HV sampler

Lin et al. [5] demonstrated the method performance of the new PFASs sampler (FM4) and absorbent (GAIACTM) and showed good recoveries for the majority of targeted compounds. In this study, we compared the concentrations of PFASs collected by the new FM4 sampler and the conventional HV sampler. Mean values of the ratio of the concentrations of PFCAs (0.67–1.2) and PFSAAs (0.55–0.92) of FM4 sampling method to those of HV sampling method indicated the comparability of these method. Compared to the conventional HV sampler, the new FM4 sampler had the advantages of a better method recoveries and a lower ion suppression in LC-MS/MS analysis (data not shown). Due to the gas-particle partitioning and portability, the FM4 sampler enables us to assess the contamination level and phase distribution of PFASs at several monitoring sites.

4.2 Atmospheric concentrations of PFASs in Osaka, Japan

The goal of our project is monitoring and characterization of PFASs contaminations in atmosphere and river water at various regions in Japan for risk profiling. In this study, we demonstrated the quantification of 30 PFASs in the atmosphere in Osaka, Japan. Figure 4 shows the atmospheric concentrations of PFOA and PFOS for ten years during the warm season in Japan that were measured by the HV sampling techniques [3]. The concentrations of PFOA and PFOS in our study were within the ranges of the previous monitoring results (PFOA: 1.9–260 pg/m³, PFOS: 0.52–14 pg/m³). The sum of the concentrations of ionic PFASs in Osaka metropolitan area was higher than those in suburban area in Japan (11 pg/m³) [4] and oceanic and coastal area in East Asia (18–33 pg/m³) [6].

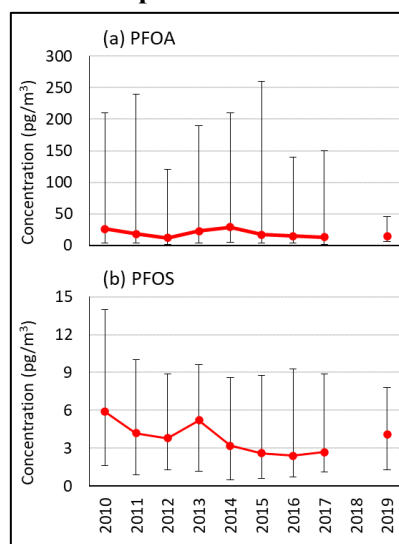


Figure 4: Atmospheric concentrations of PFOA (a) and PFOS (b) during warm season in 2010–2019 in Japan [3]. Red dot is median value. Error bars represent ranges of values ($n=35-37$).

However, the sum of the concentrations of ionic PFASs in suburban and urban areas (Tokyo) in Japan (220–680 pg/m³, excluding C2 and C3 PFASs) reported by other study [5] were relatively similar to our results. These results suggest that a wide variety of PFASs concentrations among regions and seasons in Japan.

The gas-particle partitioning of PFASs was important parameter to predict its environmental fate. The increase in the particle associated fractions of PFCAs with the increasing length of carbon chain should represent their vapor pressure. The particle-associated fractions of PFASs observed in this study were lower than those reported in Lin et al. (e.g., PFOA: 0.124 ± 0.078, PFOS: 0.417 ± 0.083) [5]. Because of the lower particle-associated fractions of PFASs, the most of the ionic PFASs appeared to be distributed in gas phase in the atmosphere in Osaka. However, it is also considered that precursors of PFCAs, such as fluorotelomer alcohols (FTOHs) [7], were adsorbed to PUF or activated charcoal fiber and then oxidized to PFCAs during sampling period. In fact, the sum of the concentrations of FTOHs in Osaka city (53–1200 pg/m³) [8] were significantly higher than those in outdoor air reported in Lin et al. (70–290 pg/m³) [5].

5 Conclusions

We observed the 30 ionic PFASs in the atmosphere in Osaka, Japan using a newly developed PFASs sampler (FM4) and absorbent (GAIACTM). Regarding the ionic PFASs, the results of the FM4 sampler were comparable to those of the conventional HV sampler. The differences in the concentrations and gas-particle partitioning of the PFASs between our observation and the previous report suggested a wide variety of the contamination characteristics of PFASs among regions and seasons in Japan. Although topics seem to be shifting to emerging PFASs recently, it is also important to understand the distributions of the regulated legacy PFASs, because it is still incomprehensible.

6 Acknowledgments

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7 References

1. Smithwick, M., Mabury, S. A., Solomon, K. R., Sonne, C., Martin, J. W., Born, E. W., Dietz, R., Derocher, A. E., Letcher, R. J., Evans, T. J., Gabrielsen, G. W., Nagy, J., Stirling, I., Taylor, M. K., Muir, D. C. G. (2005). Circumpolar Study of Perfluoroalkyl Contaminants in Polar Bears (*Ursus maritimus*). *Environ. Sci. Technol.*, 39(15), 5517–5523. <https://doi.org/10.1021/ES048309W>
2. Fenton, S. E., Ducatman, A., Boobis, A., DeWitt, J. C., Lau, C., Ng, C., Smith, J. S., Roberts, S. M. (2021). Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research. *Environ. Toxicol. Chem.*, 40(3), 606–630. <https://doi.org/10.1002/ETC.4890>
3. Ministry of the Environment Government of Japan, *Report on Environmental Survey and Monitoring of Chemicals*, <https://www.env.go.jp/chemi/kurohon/en/index.html> (2022/7/10 accessed)
4. Wu, R., Lin, H., Yamazaki, E., Taniyasu, S., Söregård, M., Ahrens, L., Lam, P. K. S., Eun, H., Yamashita, N. (2021). Simultaneous analysis of neutral and ionizable per- and polyfluoroalkyl substances in air. *Chemosphere*, 280, 130607. <https://doi.org/10.1016/J.CHEMOSPHERE.2021.130607>
5. Lin, H., Taniyasu, S., Yamazaki, E., Wu, R., Lam, P. K. S., Eun, H., Yamashita, N. (2022). Fluorine mass balance analysis and per- and polyfluoroalkyl substances in the atmosphere. *J. Hazard. Mater.*, 435, 129025. <https://doi.org/10.1016/J.JHAZMAT.2022.129025>
6. Yamazaki, E., Taniyasu, S., Wang, X., Yamashita, N. (2021). Per- and polyfluoroalkyl substances in surface water, gas and particle in open ocean and coastal environment. *Chemosphere*, 272, 129869. <https://doi.org/10.1016/J.CHEMOSPHERE.2021.129869>
7. Ellis, D. A., Martin, J. W., de Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P., Wallington, T. J. (2004). Degradation of Fluorotelomer Alcohols: A Likely Atmospheric Source of Perfluorinated Carboxylic Acids. *Environ. Sci. Technol.*, 38(12), 3316–3321. <https://doi.org/10.1021/ES049860W>
8. Tojo, T., Asakawa, D., Ichihara, M., Taniyasu, S., Hanari, N., Yamashita, N. (2022), Survey of neutral PFASs in ambient air using FM4 air sampler, *ibid*.