

Survey of Neutral PFASs in Ambient Air Using FM4 Air Sampler

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1 Introduction

Some reports have revealed that perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) have been detected in animals living in remote areas such as the Arctic, Antarctic, and the middle of the North Pacific Ocean [1], and the global spread of contamination is known. At first, PFOS and PFOA were not expected to be transported long distances by air because of their low volatility and moderate water solubility [2]. However, subsequent studies have calculated that global movement and diffusion of PFOS and PFOA may be caused by involvement of volatile and semi-volatile precursors [3].

A variety of substances are reported to be present as intermediates in commercially produced PFOA [4-5], and fluorotelomer alcohols (FTOHs) are among the volatile precursors present in the environment. In previous study [6], 8:2FTOH were detected in ambient air at extremely high concentrations in the Keihan area in Japan, including Osaka City, compared to other areas, suggesting the influence of large-scale sources. Since they are present in trace amounts in the environment, highly sensitive analysis is required for their detection.

Analysis of perfluoroalkyl compounds (PFASs) in ambient air is generally performed by LC-MS (or LC-MS/MS) for ionic PFASs, including PFOS and PFOA, and GC-MS (or GC-MS/MS) for neutral PFASs of volatile and semi-volatile substances such as telomers. Therefore, there are very few reported cases of simultaneous analysis of ionic and neutral PFASs. Since securing power supply and location (area) is important for air sampling, it is desirable to measure ionic PFASs and neutral PFASs in the same sample, if possible, by collecting them using the same collection equipment and fractionating or separating the sample. By doing so, the relationship between PFOA (ionic PFASs) and FTOHs (neutral PFASs), which are considered to be one of their precursors, can be clarified, and if a high concentration event occurs, it is expected to be easier to determine the cause.

We conducted environmental survey of PFASs in ambient air in the Osaka city area using FM4 air sampler, which is capable of simultaneously collecting ionic and neutral PFASs. Simultaneous measurements of the FM4 method and high volume air sampler (HV) method, which is used in the Environmental Survey and Monitoring of Chemicals conducted by Ministry of the Environment Government of Japan, were performed to verify the usefulness of the FM4 method. The results of neutral PFASs among PFASs will be reported in this abstract. Under the EPA's 2010/15 PFOA Stewardship Program [7], the world's major fluoropolymer manufacturers are committed to making efforts to eliminate PFOA and related substances with higher carbon numbers than C8 by 2015. One of the objectives of this study was to confirm the disappearance of FTOHs, one of the precursors of PFOA, by comparing the results of the pre-2015 survey with the current results.

2 Materials and Methods

The HV method is an existing technique for environmental investigation of PFASs (PFOS and PFOA) in ambient air. In this method, HV equipped with quartz fiber filter, PUF, and active carbon fiber filter is used to collect ambient air at a flow rate of 100 L/min or higher. FM4 method can classify particles into three sizes (>10 µm (first stage), 2.5 to 10 µm (second stage), and 1.0 to 2.5 µm (third stage)) at a flow rate of 20 L/min. FM4 is equipped with quartz fiber filter, PUF, and fibrous activated carbon filters (GAIAC) and low volume air sampler (LV) to collect ambient air [8]. In this study, we have investigated more than 30 substance groups based on ISO 21675, of which 18 are neutral PFASs (Table 1). Surveys were conducted on the roof of Osaka City Research Center of Environmental Sciences three times during September and October (warm season) and January and February (cold season), respectively. Extraction of quartz fiber filter, PUF, and fibrous activated carbon filters were all performed with 50% dichloromethane/ethyl acetate. The eluate was concentrated under nitrogen gas flow to a final volume for instrumental analysis. Quantitation and identification of neutral PFASs were determined by GC-MS/MS (Agilent Technologies: 7010 TripleQuad GC/MS). Quantification was performed by internal standard method for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, N-MeFOSE, and N-EtFOSE, and by absolute calibration curve method for the others.

Table1 Target Compounds

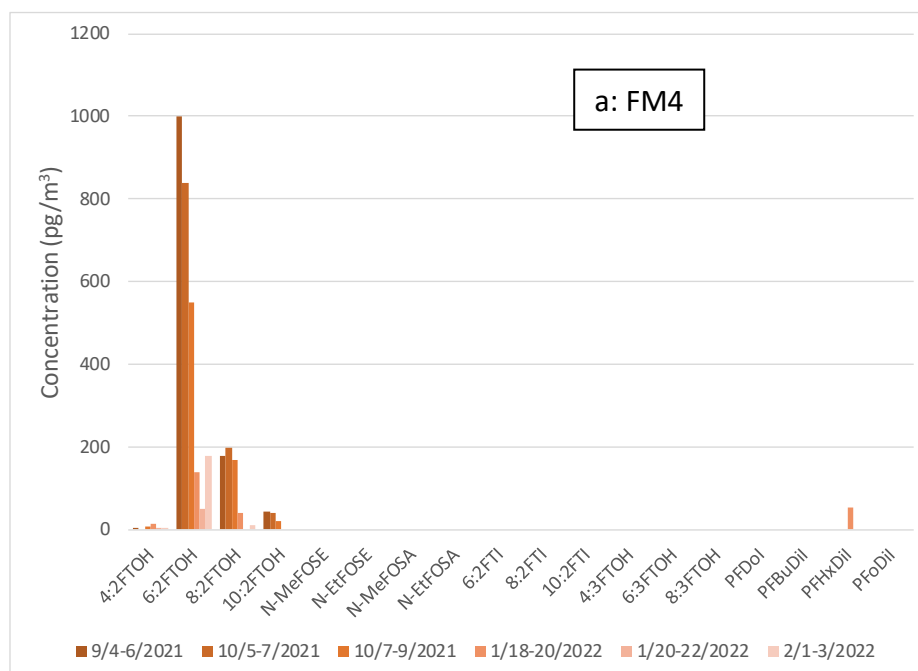
Fluorotelomer alcohol (FTOHs)	4:2 FTOH, 4:3 FTOH*, 6:2 FTOH, 6:3 FTOH*, 8:2 FTOH, 8:3 FTOH*, 10:2 FTOH
Perfluorooctanoic sulfonamide ethanol (FOSEs)	N-MeFOSE, N-EtFOSE
Perfluorooctanesulfonamide (FOSAs)	N-MeFOSA*, N-EtFOSA*
Fluorotelomer iodine (FTIs)	6:2 FTI*, 8:2 FTI*, 10:2 FTI*
Fluorinated iodine alkanes (PFDoI)	PFDoI*
Fluorinated diiodoalkanes (FDIAs)	PFBuDiI*, PFHxDiI*, PFOdiI*

* cold season only

3 Results and Discussion

Six compounds were measured during the warm season (September-October) and 18 compounds during the cold season (January-February), of which 5 (4:2, 6:2, 8:2, or 10:2 FTOH and PFHxDiI) were detected. The results are shown in Figure1 (Upper). The total concentrations of PFASs (the sum of 6 (warm season) and 18 (cold season) congeners) in ambient air using FM4 air sampler were in a wide range (mean) of 53 to 1200 pg/m³ (590 pg/m³). PFASs concentrations during the warm season tended to be higher than during the cold season.

Four of the five compounds detected were telomer alcohols such as 6:2FTOH and 8:2FTOH. Wu et al. [9] conducted a study on PFASs in ambient air in Tsukuba city, Japan, and reported that FTOHs were dominantly detected among 19 neutral PFASs, with 6:2FTOH concentrations accounting for 40% and 8:2FTOH for 32% of total neutral PFASs concentrations. PFOA is a compound covered by the Stockholm Convention on Persistent Organic Pollutants (POPs), and one of its volatile precursors is FTOHs. FTOHs are primary alcohols characterized by two non-fluorinated carbons adjacent to a hydroxyl group. In particular, FTOHs that were detected frequently in this survey were those with carbon chains that were multiples of 2 and represented as 4:2, 6:2, 8:2, or 10:2 FTOH, depending on the ratio of the number of fluorinated and non-fluorinated carbons. Many of these compounds are formed in telomerization process used in manufacturing plants, are used in large quantities in industry, and are frequently detected in products such as water and oil repellents for textiles. Among them, 6:2FTOH was detected in all samples and showed higher concentration levels than other FTOHs. Prior to this study, surveys of FTOHs in ambient air were conducted in Osaka city area in February 2011 and March 2017 [10]. The results of those studies suggest that various international efforts, including the EPA's 2010/15 PFOA Stewardship Program, have reduced emissions to air of 8:2FTOH and 10:2FTOH, which are related compounds of PFOA with higher carbon numbers than C8. On the other hand, 6:2FTOH, which is considered to be a substitute for 8:2FTOH, has been found to have increased significantly. The results of this study are similar to those of approximately five years ago. In addition, 4:2FTOH, which was not detected in the 2011 and 2017 surveys, was detected, suggesting a shift to alternatives with shorter carbon chain lengths.



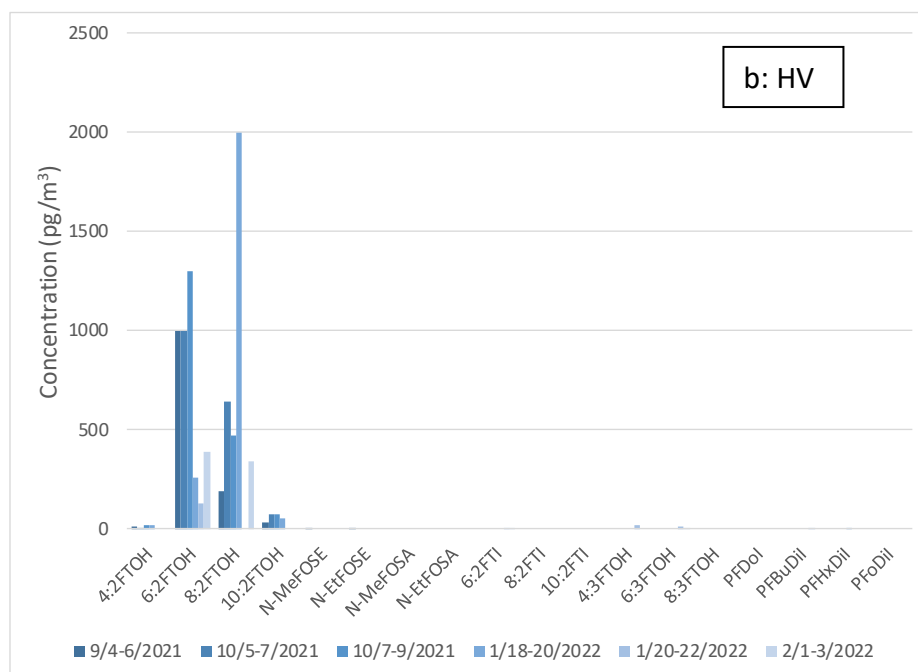


Figure 1: Neutral PFASs concentrations (pg/m³) in ambient air from Osaka city area (a: FM4, b: HV).

The total concentrations of PFASs (the sum of 6 (warm season) and 18 (cold season) congeners) in ambient air using HV sampler were in a wide range (mean) of 170 to 2300 pg/m³ (1300 pg/m³) (Figure1 (Lower)). Simultaneous measurements by FM4 and HV methods were performed, and the results were consistent in many respects, including the dominantly detection of FTOHs in both methods and the highest concentration of 6:2 FTOH, confirming the usefulness of the FM4 method.

4 Conclusions

Surveys for neutral PFASs in ambient air was conducted in Osaka City area using GC/MS/MS. The results suggest that emissions of 8:2FTOH and 10:2FTOH, which are related compounds of PFOA with higher carbon numbers than C8, have decreased in Osaka city area in Japan due to various international efforts, including the EPA's 2010/15 PFOA Stewardship Program, while emissions of 6:2 FTOH was found to have increased significantly.

PFOS and PFOA became regulated compounds in 2009 and 2019, respectively, under the Stockholm Convention on Persistent Organic Pollutants (POPs). Furthermore, perfluorohexanesulfonic acid (PFHxS) is also being considered as a substance for the Convention, and related substances are being added to the list of compounds to be covered by the Convention. Focusing on chemicals suspected of eventually turning into POPs will help to manage their risks over the long term, and it is important to continue to monitor their disappearance.

5 Acknowledgments

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6 References

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