FLUXES OF PERFLUORINATED CHEMICALS THROUGH PRECIPITATION IN JAPAN, USA AND SEVERAL OTHER COUNTRIES

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Abstract

The widespread occurrence of perfluoroalkyl acids (PFAs) in different environmental matrices has been documented. PFAs are present in the atmospheric environment, however, only a few studies have investigated the occurrence in precipitation. Monitoring of PFAs in precipitation is important for calculating the fluxes and depositions in the environment. In this study, precipitation samples from Japan, USA, Hong Kong, India and France were analyzed. The highest median concentration of perfluorinated compounds (PFCs) was detected in Hong Kong, China (8.77 ng/L), whereas the lowest concentration was found in Patna, India (1.11 ng/L). Concentrations of PFCs were similar in precipitation samples collected from two urban areas (Kawaguchi, Japan and Downtown Albany, USA), which showed relatively higher concentrations than those nearby residential/suburban areas (Tsukuba, Japan and Slingerlands, USA). Perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) were found to be the two dominant PFCs in precipitation samples from Japan and the USA, reflecting that these compounds might share some common sources of contamination. The estimated annual fluxes of PFCs in Japan and the USA were consistent with the concentrations of fluorotelomer alcohols reported in other studies. Precipitation appears to be an effective scavenger of PFCs in the atmospheric environment.

Introduction

Perifluorinated compounds (PFCs), especially perfluoroalkyl acids (PFAs), including perfluoroalkylsulfonic acids (PFASs) and perflurocarboxylic acids (PFCAs), are found to be globally distributed in various environmental matrices[1-4]. Owing to their high water solubility, aquatic ecosystem is thought to be a major sink for these compounds and analyses of trace level of PFAs have been conducted in drinking water[5] and ocean surface water[6]. Pathways of transport of PFAs, namely hydrospheric and atmospheric mechanisms have been suggested[7]. Precipitation is an important matrix to investigate the environmental fate and atmospheric transport of these pollutants in the environment.

Evidences suggest the presence of PFAs in the atmospheric environment[8-15]. Release of PFCAs (e.g. perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA)), which are used as processing aids in fluoropolymer manufacturing[8,9] is a direct source of entry into the environment. Volatile fluorinated organic compounds such as fluorotelomer alcohols (FTOHs) have been found in Asian and Western US air masses[10], and precipitation from Japan[11]; fluorotelomer carboxylic acids (FTCAs) and fluorotelomer unsaturated carboxylic acids (FTUCAs) were found in rainwater from North America[12] and Canada[13]. These volatile fluorinated precursors (e.g. FTOHs) may be degraded into FTCAs and FTUCAs and finally to PFCAs in the atmosphere[14-15]. PFCAs and PFASs have been detected in air samples in the USA[7].

Recently, PFAs have been detected in precipitation samples in North America[12] and China[16]. Wet deposition of PFAs is an important pathway for the transfer of these compounds from air to soil or plants. Measurement of PFC concentrations in precipitation can enable understanding of fluxes and depositions of PFAs in the environment. In light of this, precipitation samples from Japan, USA, Hong Kong, India and France, during 2006-2008, were analyzed.

Materials and Methods

Precipitation samples were collected from Tsukuba (*n=15*) and Kawaguchi (*n=16*) in Japan, Downtown Albany (*n=6*) and Slingerlands (*n=6*) in the US, Hong Kong (*n=5*) in China, Patna (*n=2*) in India and Toulouse (*n=2*) in France during 2006-2008. Details of the sampling locations in Japan and the USA are shown in Table 1.

Table 1. Characteristics of the sampling locations in Japan and the US.

	Japan		USA	
Location	Tsukuba	Kawaguchi	Slingerlands	Downtown Albany
Area [km^2]	284.07	55.75	56.6	
Population	207,394	500,140	8,500	95,658
Characteristics	Residential Area	Industrial Area	Residential Area	Business Area

Most of the samples were collected in polypropylene (PP) bottles using a PP funnel. Another set of samples was collected at AIST, Tsukuba (n=30) from six different dates; five consecutive 100 mL samples were collected in a glass container using a rain sampler modified with fluoropolymer-free materials (Shibata Scientific Technology Ltd., Tokyo, Japan). All precipitation samples were stored at -20°C until analysis. Eighty to 100mL of precipitation samples were extracted using solid phase extraction Oasis®WAX (6cc) cartridges (Water Corp., Milford, U.S.A). The analytical procedures were similar to those reported earlier[17].

Nineteen PFCs, including perfluoroctanesulfonate (PFOS), perfluorohexanesulfonate (PFHxS), perfluorobutanesulfonate (PFBS), perfluorooctadecanoic acid (PFOcDA), perfluorohexadecanoic acid (PFHxDA), perfluorotetradecanoic acid (PFTeDA), perfluorododecanoic acid (PFDoDA), perfluoroundecanoic acid (PFUnDA), perfluorodecanoic acid (PFDA), PFNA, PFOA, perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), perfluorobutanoic acid (PFBA), perfluorooctane sulfonamide (PFOSA), *N*-ethyl perfluorooctane sulfonamide (*N*-EtFOSA), *N*-ethyl perfluorooctane sulfonamidoacetate (*N*-EtFOSAA) and 8:2 fluorotelomer unsaturated carboxylic acid (8:2 FTUCA) were quantified. Separation, identification and quantification of the analytes were performed by using an Agilent HP1100 liquid chromatography (Agilent, Palo Alto, CA) interfaced with a Micromass Quattro Ultima Pt mass spectrometer (Waters Corp., Milford, MA) using the parameters described

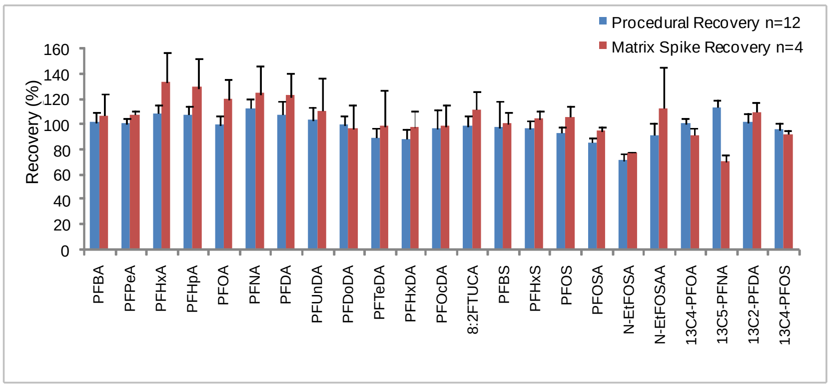

Fig 1. Procedural and matrix spike recovery of PFCs (%).

elsewhere[17,18].

Procedural blanks and recoveries of target compounds through the analytical procedure were checked with every batch of samples analyzed. Concentrations of target compounds in all procedural blanks were below the corresponding limits of quantification (LOQ) (i.e <0.05-2 ng/L). The procedural recoveries of individual PFCs ranged from 71% to 113%. Single analysis was performed for each precipitation events. Surrogate standards $^{13}C_4$-PFOS, $^{13}C_2$-PFDA, $^{13}C_5$-PFNA and $^{13}C_4$-PFOA were spiked into each sample to determine the overall recoveries of the target analytes. Result of recoveries and matrix spike recoveries are shown in Fig.1.

Results and Discussion

International Comparison of PFCs in Precipitation

Precipitation samples (*n=52*) from six cities were analyzed. Total concentrations and median concentrations of PFCs are shown in Fig. 2. Comparable concentrations were observed between Tsukuba and Kawaguchi in Japan, Downtown Albany and Slingerlands in New York, USA and Hong Kong, except for two samples from Japan which contained unusually high concentrations of PFCs. Median concentrations of PFCs in precipitation from Tsukuba, Japan (4.34 ng/L) and Slingerlands, USA (4.78 ng/L), which are both residential areas, were similar. Concentration of PFCs in Kawaguchi, Japan (7.60 ng/L) and Downtown Albany, USA (7.99 ng/L), which are both urban areas, were also similar. These results suggested that PFC concentrations can reflect the local urbanization/atmospheric contamination. The lowest median concentration of PFC (1.11 ng/L) was found in precipitation from Patna, India, which was consistent with the results of low contamination in Indian river water[19]. Limited precipitation samples were analyzed for Hong Kong and Toulouse, France, and hence further sampling is needed.

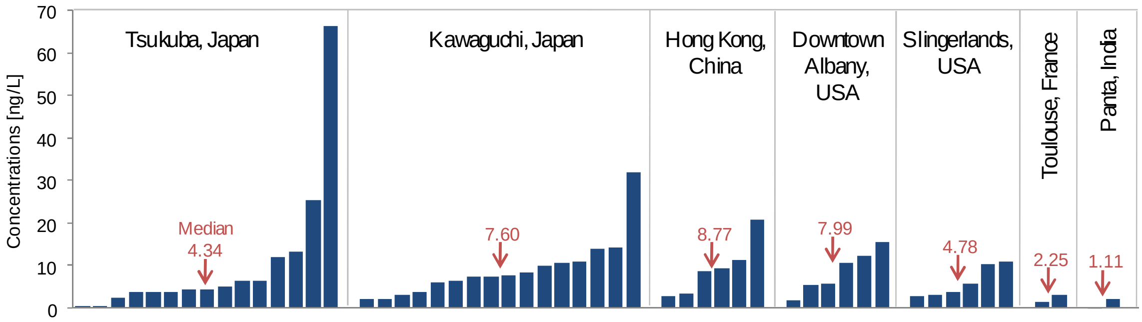

Fig. 2. International comparison of PFC concentrations [ng/L] in precipitation samples.
(Sum of PFCs = PFCAs (C_4-C_{18}) + 8:2FTUCA + PFASs (C_4, C_6, C_8) + PFOSA + *N*-EtFOSA + *N*-EtFOSAA)

Total Concentrations of PFCs in Japanese Precipitation

Precipitation samples collected for every even month from Tsukuba and Kawaguchi, Japan were analyzed for the period 2006-2008. Total PFC concentrations and the amount of precipitation are shown in Figs. 3 and 4. The lowest amounts of precipitation with the greatest concentrations of PFCs were observed in August 2006 and 2007 for both Tsukuba and Kawaguchi. A similar trend of PFC concentration was discovered in precipitation samples from Tsukuba during June 2006 to April 2008 with a dramatic decrease of total PFC concentrations was found after August, and comparable concentration of PFCs was observed in precipitation collected from October to June, 2006 and 2007. However, no clear seasonal trend was found for samples from Kawaguchi.

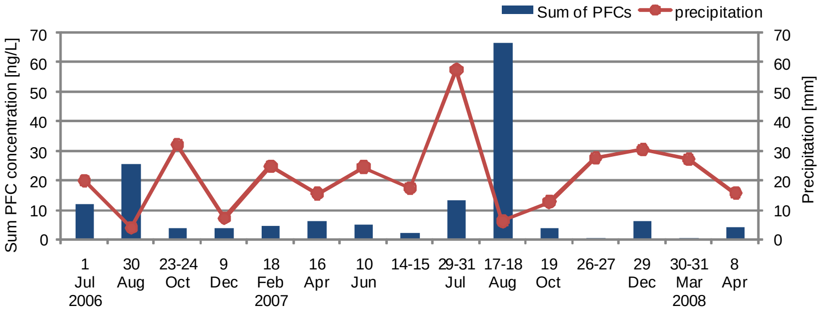

Fig. 3. Total concentration of PFCs in Tsukuba precipitation samples from June 2006 to June 2008.

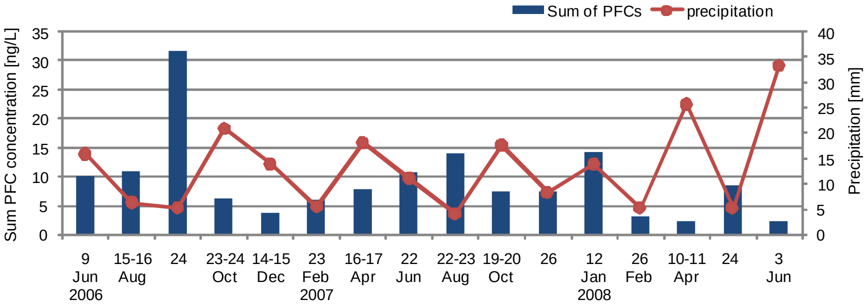

Fig. 4. Total concentration of PFCs in Kawaguchi precipitation samples from June 2006 to June 2008.

PFC Compositions of Precipitation in Japan

PFOA and PFNA were the dominant PFCs in precipitation samples from Tsukuba and Kawaguchi, Japan. A similar observation was also found for Albany, New York, USA. Different patterns were observed for PFASs especially for PFOS, PFBS and *N*-EtFOSAA from other PFCAs in some samples collected from Kawaguchi, Japan. Relatively higher concentration of *N*-EtFOSAA (1.28 ng/L) was detected in Kawaguchi (industrial area) compared to Tsukuba (residential area) (0.6 ng/L), where *N*-EtFOSAA may used in local industry.

Evidence of PFCs in Air Scavenged by Precipitation

Precipitation samples were collected at every 1 mm up to 5 mm from six different precipitation events in Tsukuba (Fig. 5). Higher concentrations of PFCs were detected in the first 1 mm of the precipitation, while a dramatic decrease in concentration was found for most of the PFCs after the first 1 mm of the precipitation. This provides evidence for scavenging of PFCs from the atmosphere by wet deposition. The rate of elimination of certain PFCs such as PFOS may different from other PFCAs, as higher concentration of PFOS may present in the 1-2 mm precipitation rather than the first 1 mm. This result indicates that there are different scavenging rates between PFCAs and PFASs, and might due to have different physiochemical properties of these classes of compounds. Further investigation is needed to clarify this point.

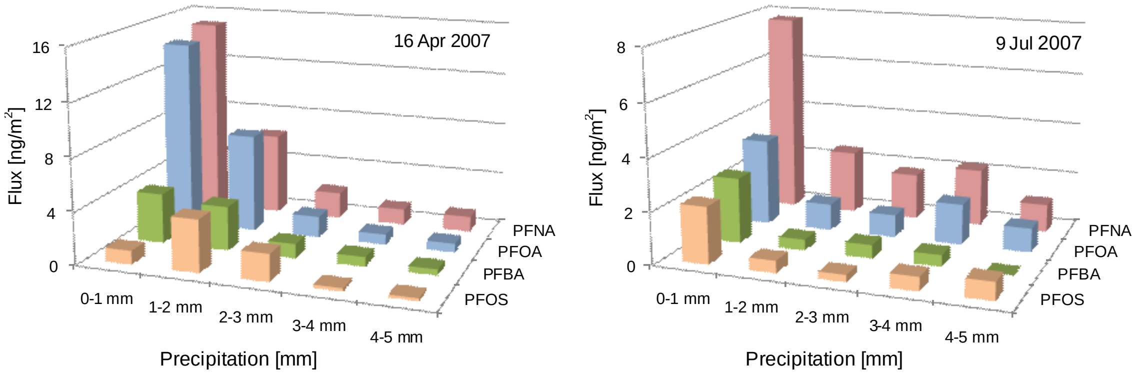

Fig. 5. Temporal reduction in PFCs in Tsukuba precipitation samples collected on 16 April 2007 and 9 July 2007

Estimated Annual Fluxes in Each Locations

Table 2 shows the estimated annual fluxes of PFCs in Japan and in the USA. Higher PFC fluxes were observed in Kawaguchi than in Tsukuba. This observation is consistent with the concentration of airborne fluorotelomer alcohols[21] detected in Japan in 2007, where higher concentration was detected in Tokyo than in Ibaraki. A decrease in the flux of both PFCAs and PFASs was also observed from June 2006 to May 2008. For USA, fluxes of PFCAs in suburban area (i.e Slingerlands) is lower than those in urban area (i.e. Downtown Albany) which is consistent with the reports that higher concentrations of FTOHs were found in the North American urban areas.[22] However, fluxes of PFASs were opposite, suggesting that there might be different atmospheric deposition pathways for PFASs, and this result also resembled that PFASs might have different scavenging rates compared to PFCAs.

Table 2. Annual fluxes [ng/m^2] of PFCs through precipitation in Japan and USA.

		Japan				**USA**	
Location		Tsukuba		Kawaguchi		Slingerlands	Downtown Albany
Year		Jun 06 - May 07	Jun 07 - May 08	Jun 06 - May 07	Jun 07 - May 08	Jun 06 - May 07	Jun 06 - May 07
Precipitation	[mm]	1,630	1,220	1,600	1,370	1,170	1,170
PFCAs flux	[ng/m^2]	10,700	8,560	12,500	8,560	6,960	8,000
(PFOA flux)		(2,620)	(1,290)	(2,900)	(2,040)	(2,050)	(2,090)
PFASs flux	[ng/m^2]	746	397	2200	1,820	611	369
(PFOS flux)		(712)	(239)	(646)	(1,620)	(401)	(255)
Total PFC flux	[ng/m^2]	11,500	8,950	14,700	10,400	7,570	8,360

(PFCAs flux = PFCAs (C_4-C_{18}) + 8:2FTUCA; PFASs flux = PFASs (C_4, C_6, C_8) + PFOSA + *N*-EtFOSA + *N*-EtFOSAA; Total PFC fluxes = PFCAs flux + PFASs flux)

References

1. Giesy J.P. and Kannan K., 2001. *Environ. Sci. Technol.*, 35, 1339-1342.
2. Yamashita N., Kannan K., Taniyasu S., Horii Y., Petrick G. and Gamo T., 2005. *Mar. Pollut. Bull.*, 51, 658-668.
3. Kannan K., Corsolini S., Falandysz J., Fillman G., Senthil Kumar K., Loganathan B.G., Mohd M.A., Olivero J., Van Wouwe N., Yang J.H. and Aldous K.M., 2004. *Environ. Sci. Technol.*, 38, 4489-4495.
4. Shoeib M., Harner T. and Vlahos P., 2006. *Environ. Sci. Technol.*, 40, 7577-7583.
5. Skutlarek D., Exner M. and Farber H., 2006. *Environ. Sci. Pollut. Res.*, 13, 299-307.
6. Yamashita N., Taniyasu S., Petrick G., Wei S., Gamo T., Lam P.K.S. and Kannan K., 2008. *Chemosphere*, 70, 1247-1255.
7. Kim S.K. and Kannan K., 2007. *Environ. Sci. Technol.*, 41, 8328-8334.
8. Prevedouros K., Cousins I.T., Buck R.C. and Korzeniowski S.H., 2006. *Environ. Sci. Technol.*, 40, 32-44.
9. Boulanger B., Vargo J.D., Schnoor, J.L. and Hornbuckle, K.C., 2005. *Environ. Sci. Technol.*, 39, 5524-5530.
10. Piekarz A.M., Primbs T., Field J.A., Barofsky D.F. and Simonich A., 2007. *Environ. Sci. Technol.*, 41, 8248-8255.
11. Mahmoud M.A.M., Karrman A., Oono S., Harada K. H. and Koizumi A., 2009. *Chemosphere*, 74, 467-472.
12. Scott B.F., Spencer C., Mabury S.A. and Muir D.C.G., 2006. *Environ. Sci. Technol.*, 40, 7167-7174.
13. Loewen M., Halldorson T., Wang F. and Tomy G., 2005. *Environ. Sci. Technol.*, 39, 2944-2951.
14. Ellis D.A., Martin J.W., De Silva A.O., Mabury S.A., Hurley, M.D., Sulbaek Anderson M.P. and Wallington T.J., 2004. *Environ. Sci. Technol.*, 38, 3316-3321.
15. Wallington T.J., Hurley M.D., Xia J., Wuebbles D.J., Sillman S., Ito A., Penner J.E., Ellis D.A., Martin J., Mabury S.A., Nielsen O.J. and Sulbaek Anderson M.P., 2006. *Environ. Sci. Technol.*, 40, 924-930.
16. Liu W, Jin H., Quan X., Sasaki K., Saito N., Nakayama S.F., Sato, I. and Tsuda S., 2009. *Environmental Pollution*, in press.
17. Taniyasu S., Kannan K., So M.K., Gulkowska A., Sinclair E., Okazawa T. and Yamashita N., 2005. *J. Chromatogr. A*, 1093, 89-97.
18. Taniyasu S., Kannan K., Yeung L.W.Y., Kwok K.Y., Lam P.K.S. and Yamashita N., 2008. *Anal. Chim. Acta.*, 619, 221-230.
19. Yeung L.W.Y., Yamashita N., Taniyasu S., Lam P.K.S., Sinha A.K., Borole D.V. and Kannan K., 2009. *Chemosphere*, 76, 55-62.
20. Oono S., Harada K.H., Mahmoud, M.A.M., Inoue K. and Koizumi A., 2008. *Chemosphere*, 73, 932-937.
21. Stock N.L., Lau F. K., Ellis D.A., Martin J.W., Muir D.C. G. and Mabury S.A., 2004. *Environ. Sci. Technol.*, 38, 991-996.