

Flux of Perfluorinated Chemicals through Wet Deposition in Japan, the United States, And Several Other Countries

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Received April 13, 2010. Revised manuscript received
August 5, 2010. Accepted August 11, 2010.

The widespread distribution of perfluorinated chemicals (PFCs) in different environmental matrices has prompted concern about the sources, fate, and transport of these classes of chemicals. PFCs are present in the atmosphere, but only a few studies have investigated their occurrence in precipitation. In this study, concentrations of 20 PFCs, including C3–C5 short-chain PFCs, were quantified using HPLC-MS/MS in precipitation samples from Japan ($n = 31$), the United States ($n = 12$), China ($n = 5$), India ($n = 2$), and France ($n = 2$). Among the PFCs measured, perfluoropropanoic acid (PFPrA) was detected in all of the precipitation samples. Average total PFC concentrations ranged from 1.40 to 18.1 ng/L for the seven cities studied. The greatest total PFC concentrations were detected in Tsukuba, Japan, whereas the lowest concentrations were detected in Patna, India. PFPrA, perfluorooctanoic acid (PFOA), and perfluorononanoic acid (PFNA) were found to be the dominant PFCs in Japanese and U.S. precipitation samples. No observable seasonal trend was found in precipitation samples from two locations in Japan. Annual fluxes of PFCs

were estimated for Japan and the U.S. and the evidence for precipitation as an effective scavenger of PFCs in the atmosphere is reported.

Introduction

Perfluorinated chemicals (PFCs) have been widely used in a variety of commercial and industrial products. They are continuously released to the environment during their production, usage, and disposal (1, 2), and several PFCs are environmentally persistent and globally distributed in both human and environmental matrices (2–8). Aquatic ecosystems are major sinks for some PFCs, especially perfluoroalkyl acids (PFA), due to their high water solubility when compared with traditional persistent organic pollutants (POPs) (1, 9).

The widespread occurrence of PFCs in environmental matrices has prompted concerns about their fate and transport in the environment. Atmospheric and hydro-spheric transport mechanisms of PFCs have been proposed (10, 11), and evidence suggests that PFAs and their precursors are present in the atmospheric environment. Release of perfluorocarboxylic acids (PFCAs), such as perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA), used as processing aids in fluoropolymer manufacturing (9), is a direct source of entry into the environment. Recently, volatile fluorinated organic precursors such as fluorotelomer alcohols (FTOHs), fluorotelomer olefins (FtOs), fluorotelomer acrylates (FtAcs), and fluorosulfonamido alcohols have been found in Japan (12) and western U.S. air masses (13); intermediate degradation products of FTOHs such as fluorotelomer carboxylic acids (FTCAs) and fluorotelomer unsaturated carboxylic acids (FTUCAs) have also been detected in precipitation samples from the U.S. (14) and Canada (15). Potential oxidation of these compounds has been observed to be one reason for the presence of PFCAs in the atmosphere (10, 16–19). Moreover, PFCs were reported to occur in air from the U.S. (20) and street dust in Japan (21).

Precipitation is one of the most effective scavengers for removal of particulates and atmospheric pollutants (22, 23). There are two types of scavenging processes by precipitation: (i) in-cloud scavenging and (ii) below-cloud scavenging (24). Scavenging of persistent organic compounds (POPs) by precipitation has also been studied (25–27). Concentrations of PFCs have been measured in precipitation samples from North America (7, 14, 20), China (28), and Northern Germany (29) using different analytical methods. High concentrations of PFCs were measured in North American and German precipitation samples. However, interestingly, perfluorooctanesulfonate (PFOS) concentrations (up to 113 ng/L) predominated in precipitation samples from Dalian, China. Differences in PFC composition profiles among regions suggest that PFC concentrations in precipitation may reflect local atmospheric contamination.

There is a need to examine concentrations of PFCs in precipitation samples worldwide (i.e., spatial differences), and removal efficiencies of PFCs by precipitation because of the lack of such information. In this study, we have examined 20 individual PFCs in precipitation samples from seven cities using a robust and sensitive analytical method (30). Because limited samples were collected from India and France, these preliminary results were included to provide additional information. To our knowledge, this is the first study to compare the geographical distribution of PFCs in precipitation samples among several countries. Furthermore, we

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TABLE 1. Detailed Information on the Sampling Locations

	Japan		United States		China	India	France
location	Tsukuba	Kawaguchi	Downtown Albany	Slingerlands	Hong Kong	Patna	Toulouse
area (km ²)	284	56	57		1,100	3,200	118
population	207, 400	500,100	95,700	8,500	6,985,200	1,698,000	451,000
characteristics	residential area	industrial area	business area	residential area	business area	agricultural area	business area

measured PFCs in rain at several time intervals to provide evidence for efficient scavenging of PFCs in the atmosphere.

Materials and Methods

Sample Collection. Fifty-two precipitation samples were collected from seven cities during June 2006 to October 2008 using PP funnels (diameter: 15 cm; funnel height: 15.5 cm; stem height: 6 cm). Details regarding the sampling locations, sampling map, and sample collection are given in the Supporting Information (SI). The sampling locations are characterized by different population densities and degrees of industrialization (Table 1). Two sampling sites (i.e., one rural area and one urban area) were selected in Japan, the U.S., and Hong Kong.

Reagents, Extraction, and Analysis. Details of the chemicals and reagents, as well as the extraction and instrumental analyses are provided in the SI. Unfiltered precipitation samples (80–100 mL) were extracted using Oasis WAX cartridges based on published methods (30, 31). PFC concentrations were analyzed by the use of high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS).

Quality Control and Quality Assurance. The quality assurance and control measures including background contamination, the limit of quantification (LOQ), calibration curve, procedural blank and matrix spike recoveries are given in the SI. In this study, concentrations found in procedural blanks were below the corresponding LOQs (0.05–0.25 ng/L). The procedural recoveries of the target PFCs ranged from 72% to 113%, while matrix spike recoveries ranged from 62% to 124% (SI, Table S2). Surrogate standards (i.e., ¹³C-labeled standard) were spiked into each sample to determine overall recovery of the target analytes, which ranged from 95% to 125%. PFC concentrations were quantified using an external calibration curve and were not corrected for the recoveries (SI).

Flux Calculation. Fluxes were calculated using the concentrations in each sample and the amount of precipitation in mm during the time interval over which the samples were collected (14).

$$\text{Flux (ng/m}^2\text{)} = \text{Concentration of sample (ng/L)} \times \frac{\text{Total volume (L)}}{\text{Area of PP funnel (m}^2\text{)}}$$

Precipitation amounts were obtained from Japan Meteorological Agency (<http://www.jma.go.jp/jma/index.html>) and Wunderground in Albany, NY (<http://www.wunderground.com/US/NY/Albany.html>).

Statistical Analyses. Normality tests (Kolmogorov–Smirnov) were performed before statistical analyses. Parametric one-way ANOVA with Holm–Sidak post hoc tests of log-transformed data was used to assess significant differences in total PFC concentrations in precipitation samples among locations. Nonparametric Spearman Rank correlation analyses were employed to determine whether there were any significant correlations among different PFCs in precipitation samples from Japan, the U.S., and Hong Kong. The significance level was set to $\alpha = 0.05$. All statistical analyses were carried out using SigmaStat 3.5.

Results and Discussion

Concentrations and Compositions of PFCs in Precipitation Samples. A total of 52 precipitation samples collected from seven cities from June 2006 to September 2008 were analyzed. Ranges and average concentrations of PFCs in precipitation samples from Japan, U.S., China, India, and France are summarized in Table S3 (SI). PFCs, dominated by C3–C12 PFCAs, were measured in all of the precipitation samples (Figure 1). PFPrA was found at the highest concentration among PFCAs for most of the precipitation samples. Besides the degradation of volatile precursors, one of the possible additional sources of PFPrA in precipitation might be related to the hydrolysis of perfluoroketone (i.e., perfluoro-2-methyl-3-pentanone) (32), which has been adopted as a fire suppression agent in recent years.

Among the 20 PFCs analyzed, 15 individual PFCs were identified in both Japanese and Hong Kong precipitation samples, whereas 12 individual PFCs were found in U.S. precipitation samples (SI, Table S4). PFPrA was detected in all of the precipitation samples. PFNA was found in all of the precipitation samples from Japan, followed by PFOA (>90%) and PFHxA (>85%). *N*-EtFOSAA was detected in a greater proportion of precipitation samples (56%) from Kawaguchi (industrial area), compared to those found for other locations (>30%) except Toulouse. PFHpA, PFOA, PFNA, and PFDA were detected in all precipitation samples from the U.S. C8–C12 PFCAs were found in all Hong Kong samples, and PFBS showed the highest frequency of occurrence (80%) in contrast to other locations. 8:2 FTUCA was detected in less than 20% of the samples from Japan and Hong Kong. PFTeDA, PFHxDA, PFocDA, and *N*-EtFOSA were not detected in any of the precipitation samples (<0.05 ng/L).

International comparison of the concentrations of total PFCs, PFCAs, PFASs, and other compounds indicated that PFC contamination in precipitation samples from the seven cities decreased in the following order: Tsukuba (arithmetic mean of total PFC concentrations: 18.1 ng/L) > Albany (15.5 ng/L) > Kawaguchi (14.0 ng/L) > Hong Kong (11.2 ng/L) > Slingerlands (9.91 ng/L) > Toulouse (3.22 ng/L) > India (1.40 ng/L) (Figure 2). Three samples from Japan (i.e., two from Tsukuba (112 and 46.3 ng/L) and one from Kawaguchi (38.1 ng/L)) contained unusually elevated concentrations of PFCs. The lowest total PFC concentration was detected in Patna, India, which was significantly lower compared to other locations except France ($p < 0.01$, ANOVA, Holm–Sidak); this concentration was 9-fold lower than that found in Tsukuba, and was consistent with results from earlier studies in India (33). PFCAs were the predominant group of PFCs measured in all precipitation samples, which may be due to their higher water solubility (PFOA: 3.4 g/L; 34) than PFASs (PFOS: 570 mg/L; 35). High concentrations of PFASs (1.05 ng/L) and other compounds (0.44 ng/L) were detected in Kawaguchi, Japan, possibly due to the high degree of local industrialization and pollution.

In terms of PFC composition, PFPrA was the predominant compound in samples from Japan, U.S., and France samples, which is consistent with the results reported for North American precipitation in 2006 (14) (Figure 3). Besides PFPrA, PFOA, PFNA, and PFBA were the three major compounds found in precipitation samples from both Tsukuba and

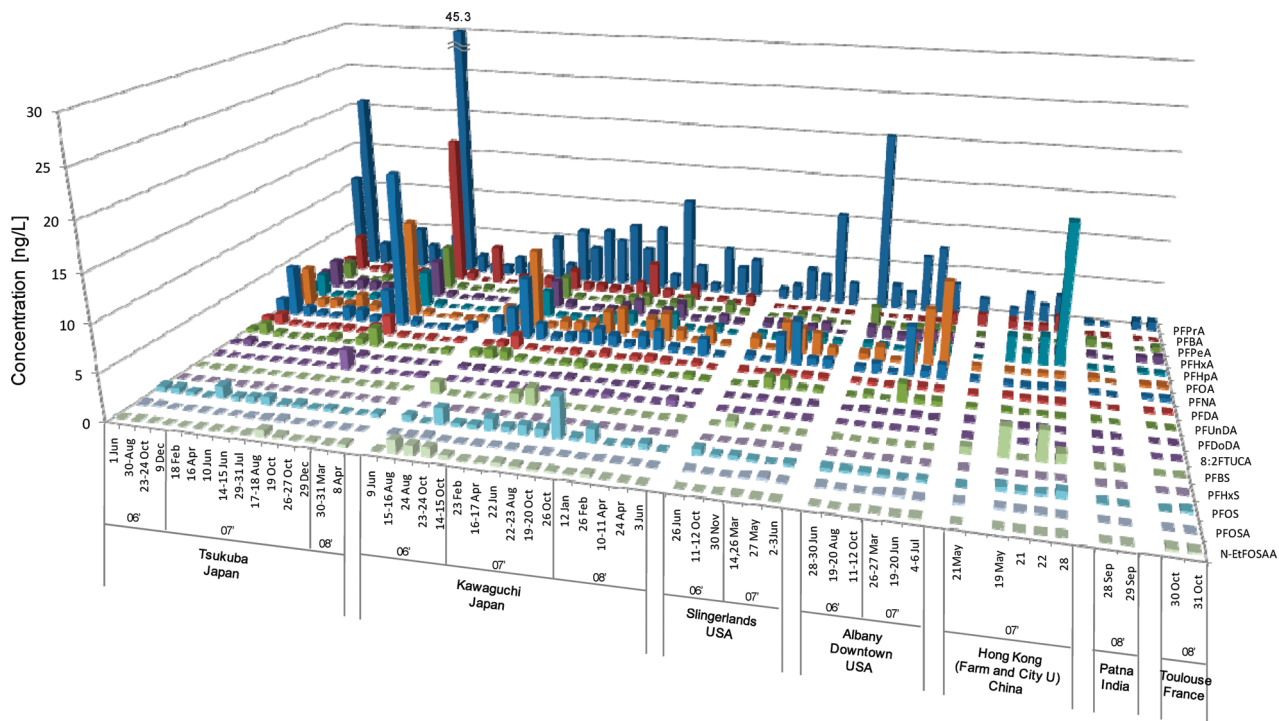


FIGURE 1. PFC concentrations in each precipitation sample from seven locations from five countries. No bar: Sample < corresponding LOQ, i.e., 0.05–0.25 ng/L.

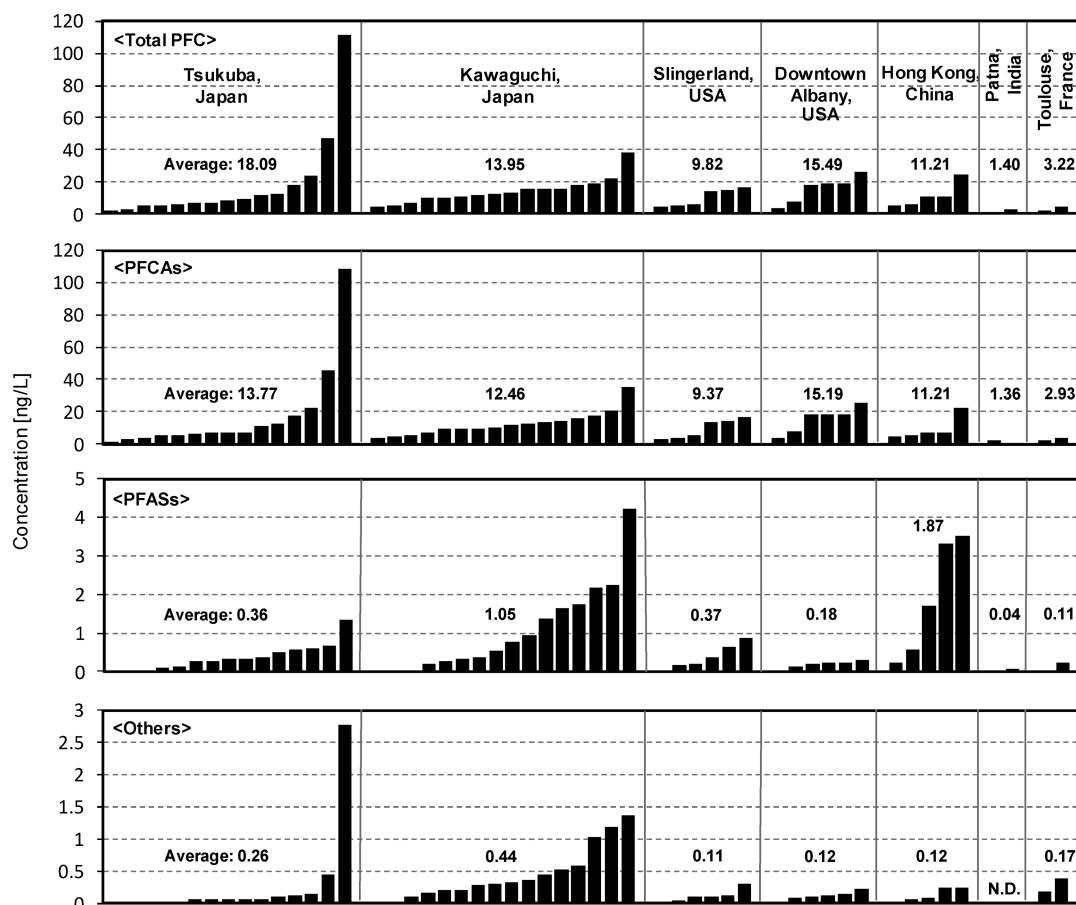


FIGURE 2. International comparison of PFC concentrations (ng/L) in precipitation samples. Total PFCs = Sum of PFCAs + PFASs + Others; Sum of PFCAs: PFCAs (C_3 – C_{12}); Sum of PFASs: PFASs (C_4 , C_6 , C_8); Others: 8:2 FTUCA, PFOSA, *N*-EtFOSAA. N.D.: Not detected. No bar: Sample < corresponding LOQ, i.e., 0.05–0.25 ng/L.

Kawaguchi. PFOA was also found to be the dominant PFC among C_8 – C_{11} PFCs in Tokyo street dust samples (21).

However, higher concentrations of PFUnDA were detected in dust samples than in precipitation samples as long-chain

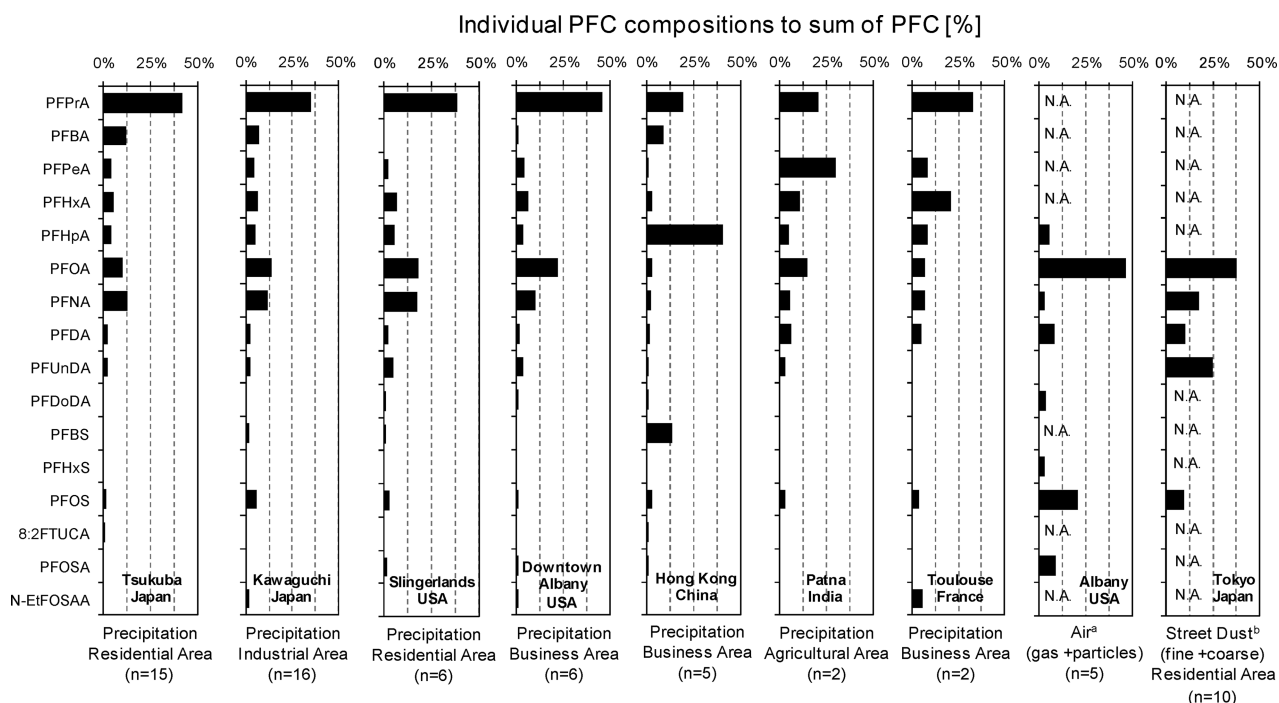


FIGURE 3. Composition profiles of individual PFC in precipitation samples. N.A.: Not analyzed; References: a, ref 20; b, ref 21.

compounds might tend to strongly adsorb onto particles. PFBA was found at a greater concentration in the precipitation samples from Japan than in other countries, which is consistent with the results of river water from Ibaraki and Saitama (36), suggesting that precipitation is one of the contamination sources in river water. PFBS, PFOS, and *N*-EtFOSAA contributed more to total PFCs in precipitation samples from Kawaguchi (industrial area) than Tsukuba (residential area). The occurrence of these chemicals may be related to their releases from local industries and the results are consistent with the detection of higher concentrations of PFASs in industrial areas in Japan (Figure 2). PFPrA, PFOA, and PFNA were the major PFCs found in precipitation samples from Slingerlands and Albany, NY (U.S.), accounting for more than 70% of the total PFCs. PFOA concentration was also high in air samples from Albany (20). The precipitation samples from Japan and the U.S. shared similar PFC composition profiles with relatively high proportions of PFPrA, PFOA, and PFNA. Production sites of ammonium perfluorooctanoate (APFO) and ammonium perfluorononanoate (APFN) are located in both the U.S. and Japan (9) which may lead to a higher proportion of PFOA and PFNA in the precipitation samples. PFBA and PFHxA, which were the fourth most dominant PFCs in Japan and U.S., respectively, are two common replacements for PFOA in recent years (37, 38). Different PFC composition profiles were observed in the precipitation samples from Hong Kong with PFHpA, PFPrA, and PFBA accounting for 33%, 22%, and 12% of the total PFC concentrations, respectively. Hong Kong does not have any PFC-related industries, and thus the sources of PFC contamination may be due to releases from adjacent industrialized areas such as Guangdong, China (39). Manufacturing of plastic products and electrical and electronic equipment would potentially involve the use of various PFCs and result in the release of these compounds into the environment, leading to a different PFCA contamination pattern and a higher proportion of PFBS being detected compared to other locations. Short-chain PFCs, such as PFPrA, PFPeA, and PFHxA, were the three dominant PFCs present in samples from Patna and Toulouse. Because limited samples were analyzed for India and France, these prelimi-

nary data may be used for the development of further monitoring studies.

Source Determination of PFCs in Precipitation Samples from Japan, the U.S., and Hong Kong. Correlation analyses were performed among individual PFCs in precipitation samples from Japan, the U.S., and Hong Kong for source determination (Table S5, SI). Significant positive associations ($p < 0.05$) were observed among most of the PFCAs in precipitation samples from Tsukuba and Kawaguchi in Japan (Table S5a–b). Positive correlations between PFCAs suggested the presence of common contamination sources from the Japanese environment in precipitation samples. PFCAs and PFOS may have different contamination sources as no significant associations were found among these compounds. PFOA and PFNA were strongly correlated with each other (Tsukuba: $r = 0.90$; Kawaguchi: $r = 0.788$, $p < 0.0001$), however no significant correlation was found between either PFOA or PFNA with 8:2 FTUCA, an oxidative product of atmospherically transported 8:2 FTOH, and therefore the contamination sources in Japan may not be attributable to the degradation of the volatile precursors (FTOHs) which was considered to be one of the indirect sources (10). In contrast, no significant correlations were observed among most of the PFCs in precipitation samples from Slingerlands, Albany Downtown in U.S. and Hong Kong (Table S5c–e), which is very different from the pattern found in Japan. These results suggested that precipitation in these locations may have distinct contamination sources such as seasonal PFC emissions and usage of different PFC-related products. PFNA and PFUnDA may have the same contamination sources in both Slingerlands and Albany Downtown in the U.S., as they were the only pair of PFCs observed to be correlated ($p < 0.05$) with each other in both locations.

Seasonal Trends in Concentrations of PFCs in Precipitation Samples from Japan. Precipitation samples collected bimonthly (i.e., February, April, June, August, October, and December) between 2006 and 2008 from Tsukuba and Kawaguchi, Japan were analyzed, and seasonal variations in PFC concentrations in precipitation samples and corresponding meteorological conditions (SI, Table S6) were examined (Figure 4). No clear seasonal trends were found

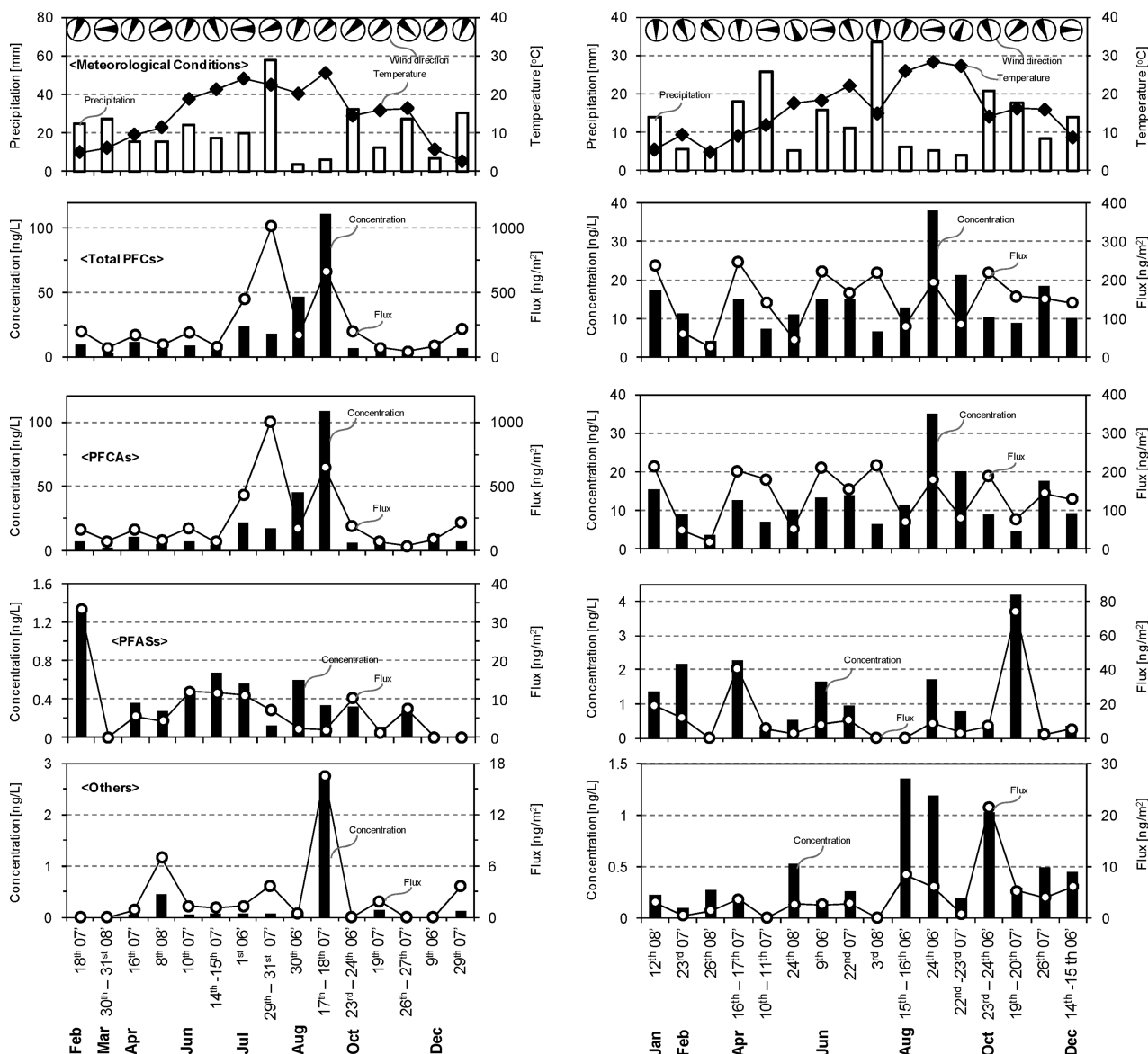


FIGURE 4. Seasonal variation of PFCs in precipitation samples from Tsukuba and Kawaguchi, Japan. Precipitation events are grouped by month on the x-axis for the period of June 2006 to June 2008. □: Precipitation (mm); -♦-: temperature (°C); ○ with arrow: wind direction (e.g., from north); ■: concentration (ng/L); ○-: flux (ng/m²). Total PFCs = Sum of PFCA + PFAS + Others; Sum of PFCA: PFCA (C₂–C₁₂); Sum of PFAS: PFAS (C₄, C₆, C₈); others: 8:2 FTUCA, PFOSA, *N*-EtFOSAA. No bar: Sample < corresponding LOQ, i.e., 0.05–0.25 ng/L.

for both locations in Japan, which is similar to the results of earlier studies (14) in three northeastern U.S. locations showing a lack of seasonal trend for PFOA and PFNA fluxes. Elevated total PFC and PFCA concentrations were found in samples collected in August in Tsukuba and Kawaguchi; however, no such trend was observed for PFASs. The composition profiles of PFCs varied depending on the month of sampling, probably because of seasonal differences in the usage pattern of PFCs.

Several parameters including precipitation amount, frequency, temperature, wind direction, and atmospheric concentrations of PFCs can influence the concentration of PFCs in precipitation. In our study, higher concentration of PFCA was found when the amount of precipitation was small (e.g., mid and late August in Tsukuba and Kawaguchi). No temperature-related seasonal trend was observed for all PFCs at both locations. Moreover, no generalization could be made about the relationship between wind direction and concentrations of PFCs at each of the rain events. The fluctuating

concentrations of PFCs and differences in composition profiles of PFCs at different precipitation events may be governed by meteorological conditions and other factors (e.g., traffic conditions, industrial activities). This hypothesis was further supported by the results from the precipitation samples from the U.S., where no seasonal trends were found from samples collected from Slingerlands and Albany.

Overall, our results suggested that PFC concentrations in precipitation are affected by the dilution process as evidenced by lower concentrations when the amount of precipitation was high. Differences in the composition of PFCs in precipitation at various locations suggested that precipitation reflects primarily local sources of contamination.

Estimated Annual Fluxes of PFCs in Japan and the United States. Annual fluxes of individual PFCs were estimated from the concentration and amount of precipitation for the samples collected in Japan and the U.S. (Table 2). A decrease in total PFC fluxes was observed in both locations in Japan. For Tsukuba (residential area), fluxes for

TABLE 2. Annual Fluxes (ng/m²) of PFCs through Precipitation in Japan and the United States^a

location	Japan				United States	
	Tsukuba		Kawaguchi		Slingerlands	Downtown Albany
	Jun 2006–May 2007	Jun 2007–May 2008	Jun 2006–May 2007	Jun 2007–May 2008	Jun 2006–May 2007	Jun 2006–May 2007
precipitation (mm)	1,630	1,220	1,600	1,370	1,170	1,170
PFPrA	10,510	4,530	8,380	6,150	3,810	9,020
PFBA	1,280	2,030	1,420	1,660	<LOQ	<LOQ
PFPeA	676	696	826	808	219	857
PFHxA	1,590	659	1,350	1,020	834	1,050
PFHpA	1,050	579	1,130	837	627	534
PFOA	2,620	1,290	2,910	2,040	2,050	2,090
PFNA	2,060	2,180	3,160	1,380	2,070	2,320
PFDA	655	448	533	297	243	297
PFUnDA	552	465	741	328	456	794
PFDoDA	200	42	120	53	37	55
PFBS	<LOQ	<LOQ	588	<LOQ	78	<LOQ
PFHxS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFOS	712	239	646	1,620	401	255
8:2FTUCA	14	173	22	135	<LOQ	<LOQ
PFOSA	30	20	160	20	130	110
N-EtFOSAA	30	20	160	20	130	110
PFCAs	21,100	12,900	20,600	14,600	10,300	17,000
PFASs	710	239	1,230	1,620	479	255
others	30	20	160	20	130	110
total PFCs	22,000	13,500	22,800	16,500	11,000	17,900

^a Total PFCs = sum of PFCAs + PFASs + others; sum of PFCAs: PFCAs (C₃–C₁₂); sum of PFASs: PFASs (C₄, C₆, C₈); others: 8:2 FTUCA, PFOSA, N-EtFOSAA.

C₃, C₆–C₁₂ PFCAs, and PFOS were lower in June 2006–May 2007 compared to Jun 2007–May 2008, while PFBA flux increased by 2-fold during that period. In Kawaguchi (industrial area), C₉–C₁₂ PFCAs fluxes decreased by 2-fold, while PFOS flux increased 3-fold between these two time periods. Comparable annual fluxes of each PFC were observed in both Slingerlands (residential area) and Albany (commercial area), NY, during June 2006 to July 2007. However, PFPrA and PFPeA fluxes were 2- and 4-fold, respectively, higher in Albany than in Slingerlands, while PFOS flux was 2-fold higher in Slingerlands than in Albany. In comparison to an earlier study (14), annual PFOA and PFNA fluxes increased 10–20 times during 1998 to 2007, suggesting increasing production and usage of PFC-related products in and near Albany (9). But, no similar data are available for Japan. The estimated annual PFC fluxes in Japan and the U.S. were also consistent with the concentrations of FTOHs reported in other studies (12, 40) in that higher concentrations were detected in urban areas than in rural areas.

Precipitation as a Scavenger of PFCs from the Atmosphere. Continuous 2–3 day precipitation samples from Tsukuba and Kawaguchi were analyzed. Higher concentrations of total PFCs were found in the first rain event even when a larger precipitation volume was collected compared to the following (second) rain event (Figure 5). PFCs are water-soluble organic acids that can dissolve in cloud droplets and also adsorb to the surfaces of the particulates in the atmosphere. The reason for the higher concentration of total PFCs in the first rain event is due to in-cloud scavenging (rain-out of PFCs dissolved in the cloud droplets) plus below-cloud scavenging (wash-out of PFCs present in the atmosphere). As wet deposition continues, the effect of below-cloud scavenging may decrease gradually, and the second rain event samples may be dominated by in-cloud scavenging, resulting in lower total PFC concentrations. This study

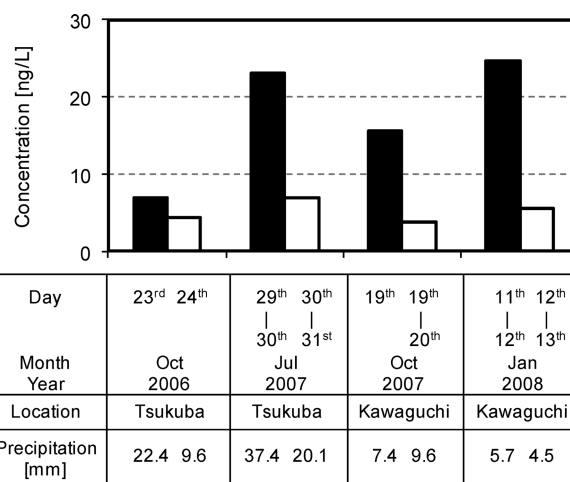


FIGURE 5. Decrease in total PFC concentrations from the first to the second rain event.

provides some initial evidence that precipitation is an effective scavenger of PFCs in the atmosphere.

Acknowledgments

We acknowledge the support by staff of City University of Hong Kong (China), AIST and Tokyo Kyuei Co. (Japan), Wadsworth Center (U.S.), Leibniz-Institute of Marine Sciences (Germany), and Patna University (India) for sample collection. The work described in this paper was partly supported by a Hong Kong AoE Project (AoE/P-04/2004) and a CityU research grant (7008035).

Supporting Information Available

Additional information, figures, and tables as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ES101170C