Polyfluorinated and Perfluorinated Chemicals in Precipitation and Runoff from Cities Across Eastern and Central China

Lijie Zhao · Meng Zhou · Tao Zhang · Hongwen Sun

Abstract Twenty-three polychlorinated and perfluorinated compounds (PFCs) were investigated in water phase and particulate matters of 19 precipitation samples (18 snow samples and 1 rain sample) from different cities across eastern and central China collected in February 2010. The PFCs in samples of 9e precipitation events during more than half a year at 1 site in Tianjin and 6 successive samples during 1 precipitation event were measured to elucidate the change of PFC in precipitation. In addition, PFCs in 3 runoffs at different kinds of sites in Tianjin were compared with those in the corresponding precipitation. The results showed that the particulate matters separated from the precipitation contained undetectable PFCs. The total PFC concentration ranged between 4.7 and 152 ng L^{-1} in water phase of the precipitation samples, with perfluorooctanoic acid (PFOA) being detected at all of the sampling sites and the dominant PFC at most of the sampling sites. Some potential precursors of environmentally concerned PFCs and their degradation intermediates were measured simultaneously, among which 6:2 fluorotelomer unsaturated carboxylic acid (6:2 FTUCA), 8:2 FTUCA, and ×(3, 4, 5, 7):3 acid [F(CF$_2$)xCH$_2$CH$_2$COOH] were measured for the first time in Chinese precipitations; however, their concentrations were all lower than the limits of detection except that 6:2 FTUCA and 8:2 FTUCA could be detected in 3 and 8 precipitation samples, respectively. No clear seasonal variation in PFC concentrations in precipitation was observed during half a year; however, a relatively greater average concentration of total PFCs was observed during winter and summer compared with spring. The concentration of individual PFCs showed an obvious descending trend in the successive samples of the precipitation event. PFOA and perfluorononanoic acid in runoffs collected from different sites showed the following similar pattern— gas station > highway > university campus—whereas the other detected PFCs had no concurrent trend.

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In recent years, perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs), with perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) as the representative compounds, have become a focus of concern because of their persistence, bioaccumulative potential (especially the homologues with a long carbon chain), and potential adverse effects on living organisms (Kannan 2011).

Fluorinated surfactants are an important class of compounds that has been used in firefighting applications, herbicide and insecticide formulations, cosmetics, greases and lubricants, paints, polishes, and adhesives (Key et al. 1997). Some main components in fluorinated surfactants, such as perfluorooctane sulfonamides (FOSAs), perfluorooctane sulfonamidoethanols, and fluorotelomer alcohols (FTOHs), are potential precursors that can be degraded in the atmosphere or under aerobic conditions to environmentally important PFCAs and PFSAs (Ellis et al. 2004; Wallington et al. 2005; Rhoads et al. 2008). As legislation became stricter for the products containing PFOS and related chemicals in developed countries, there was a production shift to other countries with less robust

environmental regulations (Risk and Policy Analysis Ltd (2004).

Precipitation is one of the most effective scavengers for the removal of particulate matters and atmospheric pollutants (Migliavacca et al. 2005; Omar Ali 2005). Organic chemicals, such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and organochlorine pesticides, were identified in precipitation samples (Franz and Eisenreich 1998; Hageman et al. 2006). Limited information (only a few reports) is available regarding PFCs in precipitation and includes Germany (Dreyer et al. 2010), North America (Scott et al. 2006; Kim and Kannan 2007; Young et al. 2007; Kwok et al. 2010), two cities in China (Liu et al. 2009a, 2009b), Japan (Taniyasu et al. 2008), India and France (Kwok et al. 2010). Among these studies, the highest concentration of PFOS was detected in the city of Dalian, China, with a geometric mean of 145 ng L^{-1} ($n = 21$) during a snow event. Hence, it is necessary to strengthen the monitoring on PFCs in precipitation in multiple areas of China.

The 6:2 fluorotelomer alcohol (6:2 FTOH) is raw material for fluorinated polymers and surfactants that replaces long-chain PFCs (Liu et al. 2010a). FTOHs were observed to undergo atmospheric degradation, which is initiated by the attack of $^{\bullet}$OH followed by oxidation, and therefore only PFCAs, FTALs [$F(CF_2)_nCH_2CHO$], and FTCAs [$F(CF_2)_nCH_2COOH$] can be formed (Ellis et al. 2004). It has been well documented that FTOH transformation in aerobic biodegradation generates two major classes of relatively stable products: PFCAs and perfluorinated x:3 acids [$F(CF_2)_nCH_2CH_2COOH$ $n = 3, 4, 5,$ or 7] (Wang et al. 2004; Wang et al. 2005, 2009; Liu et al. 2010a, 2010b). Unlike the oxidation reaction in the atmosphere, single defluorination could occur on the tertiary carbon to produce x:3 acids under the effects of multiple enzymes during biodegradation in the aquatic and terrestrial environment. Hence, these x:3 acids can only come from FTOH biodegradation and thus can be used as potential indicators of FTOH emission in the environment. Particularly 5:3 and 7:3 acids are major stable transformation products of 6:2 FTOH and 8:2 FTOH biodegradation, respectively, accounting for 11 to 15 % molar yields during 6:2 and 8:2 FTOH aerobic biodegradation in soils (Wang et al. 2009; Liu et al. 2010b).

The objective of this study was to investigate the occurrence of various environmentally concerned PFCs and their potential precursors and degradation intermediates in precipitation samples to map out the degree of contamination in China. Twenty-three analytes were monitored with a robust analytical method in 19 precipitation samples collected from different cities across the east and central China in January 2010. The monitored PFCs were PFCAs (C4-C12); PFASs (C4, C6, and C8);

some precursors, including FOSA n-methyl-FOSA (n-Me-FOSA), n-ethyl-FOSA (n-Et-FOSA), n-methyl-n-acetyl-FOSA (n-Me-FOSAA), and n-ethyl-n-acetyl-FOSA (n-Et-FOSAA); and their degradation intermediates, including 6:2 FTUCA, 8:2 FTUCA, and 3:3, 4:3, 5:3 and 7:3 acids. To our best knowledge, this is the first study to monitor 6:2 FTUCA, 8:2 FTUCA, and x:3 acids in Chinese precipitation samples. To check seasonal variations, a long-term sampling campaign was conducted at one sampling site in Tianjin during more than half a year. Moreover, consecutive 6 h sampling at intervals of 1 h was performed to characterize the removal dynamics of PFCs during a precipitation event. Three surface runoffs were also measured primarily to assess their potential contribution to PFC levels in surface water environment.

Materials and Methods

Standards and Reagents

Perfluorohexanoic acid (PFHxA [>98 %]), perfluoroheptanoic acid (PFHpA [>98 %]), and perfluoroundecanoic acid (PFUnDA [>96 %]) were purchased from Matrix Scientific (Columbia, SC). PFUnDA (95 %) and PFOS (99 %) were from Sigma–Aldrich Chemical (St Louis, MO). PFOA (>98 %) was obtained from Strem Chemicals (Bischheim, France). Perfluorononanoic acid (PFNA [>98 %]) and perfluorodecanoic acid (PFDA [>98 %]) were from Fluorochem (Derbyshire, UK). $^{13}C8$-Labeled PFOA ($^{13}C8$-PFOA) were purchased from Cambridge Isotope Laboratories (Andover, MA). Perfluorobutanoic acid (PFBA [>98 %]), perfluoropentanoic acid (PFPeA [>98 %]), sodium perfluorobutane sulfonate (PFBS [>98 %]), sodium perfluorohexane sulfonate (PFHxS [>98 %]), 6:2 FTUCA (>98 %), 8:2 FTUCA (>98 %), FOSA n-Me-FOSA n-Et-FOSA n-Me-FOSAA n-Et-FOSAA, and four kinds of internal standards (ISs [>97 %]), including $^{13}C5$-n-Et-FOSA, $^{13}C5$-n-Et-FOSAA, $^{13}C2$-8:2 FTUCA, and $^{13}C4$-Labeled sodium PFOS ($^{13}C4$-PFOS), were purchased from Wellington Laboratories (Guelph, Ontario, Canada). The x:3 acids, with >95 % purity, were provided by DuPont (Wilmington, DE). All of the standards were dissolved in methanol as stock solutions.

Methanol used for solid phase extraction (SPE) and high-performance liquid chromatography (HPLC) mobile phase was of HPLC grade, and all of the reagents used (e.g., ammonia hydroxide, ammonium acetate, sodium acetate, and acetic acid) were at least of analytical grade or greater. The solvent filters (0.22 and 0.45 μm) were from Anpel (Shanghai, China). Oasis WAX cartridges (150 mg sorbent, 6 cc; Waters, Ireland) used in SPE were from

Waters. Doubly deionized water (DDW; 18 MΩ cm^{-1}) was used throughout this work.

Sampling Campaign

Nineteen precipitation samples (18 snow samples and 1 rain sample) were collected across eastern and central China during a specific period (February 2–10, 2010). Figure 1 shows the sampling sites, which included Tianjin (snow [$n = 8$]), Hubei province (snow [$n = 2$]), Jilin province (snow [$n = 2$]), Shandong province (snow [$n = 2$]), Anhui province (snow [$n = 1$]), Hebei province (snow [$n = 1$]), Henan province (snow [$n = 1$]), Jiangsu province (snow [$n = 1$]), and Sichuan province (rain [$n = 1$]). The detail sampling meteorological conditions, particulate matter content, and chemical characteristics of the water phase (pH, salinity, and total organic carbon [TOC]) are listed in Supplementary Information Table SM 1. For seasonal variation assessment, 9 precipitation samples were obtained from 1 sampling site in Nankai district, Tianjin, on January 2 (snow), February 8 (snow), February 22 (snow), May 3 (rain), May 16 (rain), June 9 (rain), June 18 (rain), July 1 (rain), and July 9 (rain), 2010. The precipitation falling 30–150 min after the beginning of the precipitation event was collected and well mixed. Moreover, 6 rain samples were collected successively during 1 precipitation event at 1 sampling site in Nankai district, Tianjin, at intervals of approximately 1 h on June 18, 2010. Three surface runoff samples, including campus runoff, highway runoff, and gasoline station runoff, were collected from 3 sampling sites in Nankai district, Tianjin, respectively, on July 1, 2010, where the corresponding precipitation sample was collected simultaneously. The surface runoff samples were collected from rain water drains or roadside puddles.

All of the samples were collected with the containers made of polypropylene materials free of fluorine (AS ONE, Osaka, Japan), which showed no adsorption for the target chemicals in a preliminary test. Before sample collection, the containers were rinsed sequentially by methanol and DW more than twice, and a similar container filled with 500 mL DW was designed to test the travel background from Tianjin, Langfang, and Changchun, respectively. All of the samples and blank water were refrigerated immediately.

Sample Pretreatment

Snow samples were transferred to laboratory and melted at room temperature (<25 °C). All of the rain and melted snow samples were filtered through a 0.45-μm nylon filter, and the particulate matters were separated and wind-dried until constant weight before further processing. Water-phase samples and particulate matters were processed and analyzed separately. Extraction procedures used for water samples have been described elsewhere (Li et al. 2011) and were modified according to the early study (Taniyasu et al. 2005). Briefly, the water samples were extracted by SPE method with Oasis WAX cartridges using an SPE device from Supelco (Bellefonte, PA). The cartridges were preconditioned with 4 mL ammonium hydroxide in methanol and 4 mL methanol followed by 4 mL DW. A total of 500 mL of water sample was loaded onto the preconditioned cartridges with a constant flow rate of 1 drop/s. Before loading, the water phase was spiked with 5 ng ISs

Fig. 1 Map of sampling sites in eastern and central China
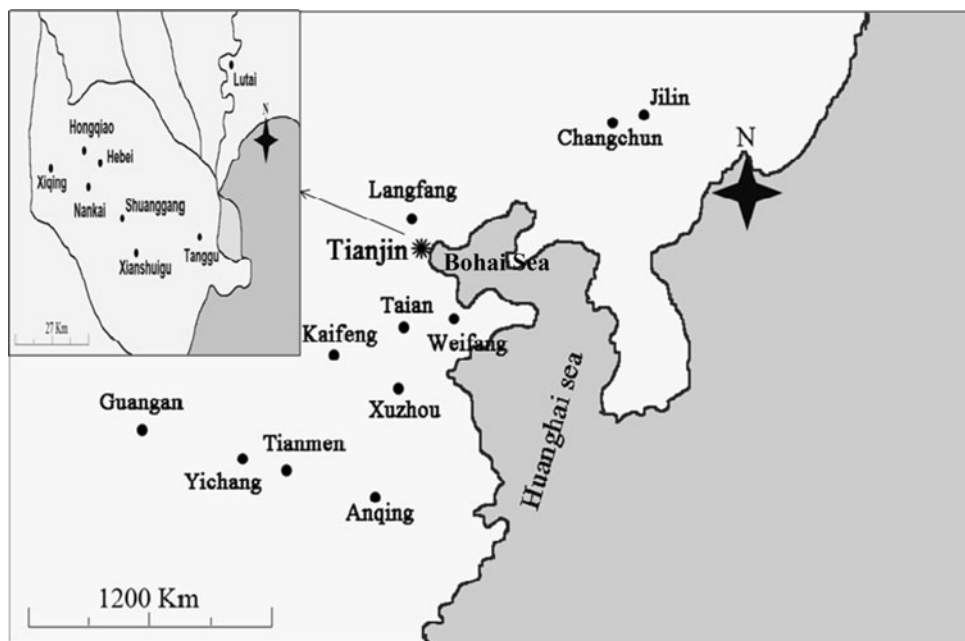
(i.e., ¹³C5-n-Et-FOSA, ¹³C5-n-Et-FOSAA, ¹³C2-8:2 FTUCA, ¹³C8-PFOA, and ¹³C4-PFOS). The cartridges were then washed with 4 mL 25 mM sodium acetate buffer (pH 4) and were dried completely under vacuum. The target compounds were eluted in 5 mL 0.1 % ammonium hydroxide in methanol poured into a polypropylene tube and was concentrated under a gentle stream of nitrogen gas to a final volume of 0.5 mL. These extracts were filtered using a 0.22-μm nylon filter into auto-sampler vials with polypropylene caps.

Air-dried particulate matters were extracted according to a previous method (Sun et al. 2011). Briefly, each particulate matter sample was spiked with 5 ng of the IS mixture. The spiked sample was first sonicated at 40 °C for 20 min in 3 mL methanol. The supernatant was removed by centrifugation at 4,200 rpm for 10 min. The residue was extracted again by 2 mL methanol according to the previously described procedure, and the two extracts were combined. After that, 30 mg Envi-Carb (Supelco) was added to the combined extraction, which was vortexed for 3 min followed by centrifugation at 4,200 rpm for 10 min. The supernatant was then decanted into a new polypropylene tube, concentrated to 0.5 mL under nitrogen gas, and filtered using a 0.22-μm nylon filter into the auto-sampler vial with polypropylene cap.

Instrumental Analysis

Analysis of the 23 target compounds was performed using an Alliance 2695 HPLC Separations Module equipped with a Quattro Micro atmospheric pressure ionization tandem quadrupole mass spectrometer (Waters, Manchester, UK), and separation was achieved using a X-Terra MS C18 column (2.1 mm id. × 150 mm, 5 μm, Waters, Ireland). The inject volume was 20 μL, and the temperature was set to 20 °C. The gradient procedure for mobile phase started at 10 % A (2.5 mM ammonium acetate in methanol) and 90 % B (2.5 mM ammonium acetate in water), which was linearly ramped to 60 % A at 0.8 min and then to 100 % at 12.8 min before reverting to the original ratio at 14.3 min; this ratio was maintained until 22.3 min. The mobile phase flow rate was 0.25 mL min⁻¹, and the column temperature was kept at 40 °C. The desolvation gas flow rate and temperature were maintained at 600 L h⁻¹ and 300 °C, respectively. The mode of multiple reaction monitoring was adopted to quantify the analytes. Other details of mass spectrometer are listed in Table SM 2.

Quality Assurance and Quality Control

Procedural blank, travel blanks, and spiked recoveries were checked to ensure the accuracy of sample analysis. Solvent blanks were run every seven to eight samples to check for baseline drift of the instrumental analysis. The limit of detection (LOD) was defined as the concentration that yielded a signal-to-noise (S/N) ratio of 3, and the limit of quantification (LOQ) was the ratio of 10 (Table SM 3). The LOQ of all of the target analytes was in the range of 0.14–4.55 ng L⁻¹ for 500-mL water samples. Five hundred milliliters of DW was extracted and processed in the same manner as the precipitation samples as the procedure blank. PFOA was detected in the procedure blank at an average level of 0.11 ng L⁻¹ ($n = 5$), which was subtracted from the concentrations of the precipitation samples, and other target analytes were not detected. The peak areas of extracted chromatograms from the three designed travel blanks were nearly identical those of the procedure blank. Matrix recovery was checked by spiking 5 ng of each of the standard analytes into the 500-mL water sample from Changchun, Jilin province (snow [$n = 3$]) and Guangan, Sichuan province (rain [$n = 3$]). The spiked recoveries of the analytes ranged from 52.8 to 106 % for snow samples and from 58.0 to 113.0 % for rain samples (relative SD [RSD] 2.2–6.3 %; Table SM 2). All of the samples were analyzed in duplicate, and each had an RSD of <15 %.

The quantization of the analytes was performed using external calibration with simultaneous matrix effect modification by ¹³C8-PFOA, ¹³C4-PFOS, ¹³C2-8:2 FTUCA, ¹³C5-n-Et-FOSA, and ¹³C5-n-Et-FOSAA. The concentrations of seven-point calibration curves ranged from 0.1 to 100 ng mL⁻¹. The correlation coefficient (r^2) of each linear calibration curve was >0.99. PFC concentrations of in precipitation samples greater than or equal to LOD but less than LOQ were considered to be a concentration half of LOQ, and those at or less than LOD were considered to be less than LOD.

## Results and Discussion

PFC Levels in Particulate Matter

The concentrations of the target analytes were all below the LOD (Table SM 2) of the analytical method in all of the 19 particulate matter samples separated from the precipitation. This was consistent with a previous study, which also reported that no PFCs were detected in particle phase of the atmosphere (Dreyer et al. 2009). Moreover, Mahmoud et al. (2009) reported that polyfluorinated telomers could be detected only in liquid phase of the rainwater, although it had low solubility. The particle-scavenging mechanism might be able to allow particulate matters to accumulate PFOA and PFOS; however, the PFCs bound to the particulate matters may be dissolved into water phase during wet precipitation. This can be explained by the high water solubility of PFOA (3.4 g L⁻¹), PFOS (570 mg L⁻¹)

(Organisation for Economic Co-operation and Development (OECD) 2002; United States EPA 2003), and other short-chain PFCAs and PFSAs. In an early study on the suspended particulate matters (SPMs) of Tokyo Bay (Ahrens et al. 2010), only approximately 3 % of total PFCs were detected in the SPM fraction, whereas 97 % were dissolved in water phase. Moreover, the amount of particulate matters filtered from precipitation samples was low (0.003–0.142 g L^{-1}, Tables SM 1 and SM 4) because only 500 mL of precipitation was acquired. Hence, it is reasonable that PFCs could not be detected in the particulate matter unless PFCs had a relatively high concentration in the atmosphere.

PFC Spatial Distribution in Precipitation from Eastern and Central China

Total PFC concentrations in precipitation samples from 19 collecting sites ranged from 4.7 to 152 ng L^{-1}. The highest concentration was detected in the city of Weifang, Shandong province. No fluorinated chemical manufactory is located in Weifang city; however, >200 textile enterprises exist in this city. Textile industry application is the most important source for fluorinated chemicals. As reported during 2004, 80 % of fluorotelomer-based commercial products was applied to carpets and textiles, whereas the remaining 20 % was used to produce fluorinated surfactants used in a variety of applications, including personal care products, leveling and wetting agents, and food-contact packaging (D'eon and Mabury 2011). Following Weifang city, three sampling sites (Xiqing, Shuanggang, Xianshuigu) in the city of Tianjin, and one sampling site in the city of Changchun, Jilin province, exhibited high concentrations of total PFCs: 89.7, 93.7, 84.1, and 92.6 ng L^{-1}, respectively. These two cities are old industrial cities in China, especially Changchun, which was one of the oldest large industrial bases in China. The city of Tianjin is an emerging industrial base, which has industrial applications of fluorinated chemicals, such as textile and electronic industry. The lowest total PFC concentration was found at the sampling site of Yichang, Hubei province. This site is located in a village with no direct emission source. These observations are consistent with the results in Japan and the United States with greater concentrations detected in urban areas than in rural areas (Kwok et al. 2010).

The concentrations of each individual PFC homologue are shown in Fig. 2. PFOA was the dominant PFC at most of the sampling sites and detected in all of the precipitation samples with concentration ranging from 0.7 to 88.0 ng L^{-1} and accounting for 5.8–75.8 % of the total PFCs at each sampling site. The highest concentration of PFOA was detected in Weifang, Shandong province, as discussed previously. Compared with the high detection
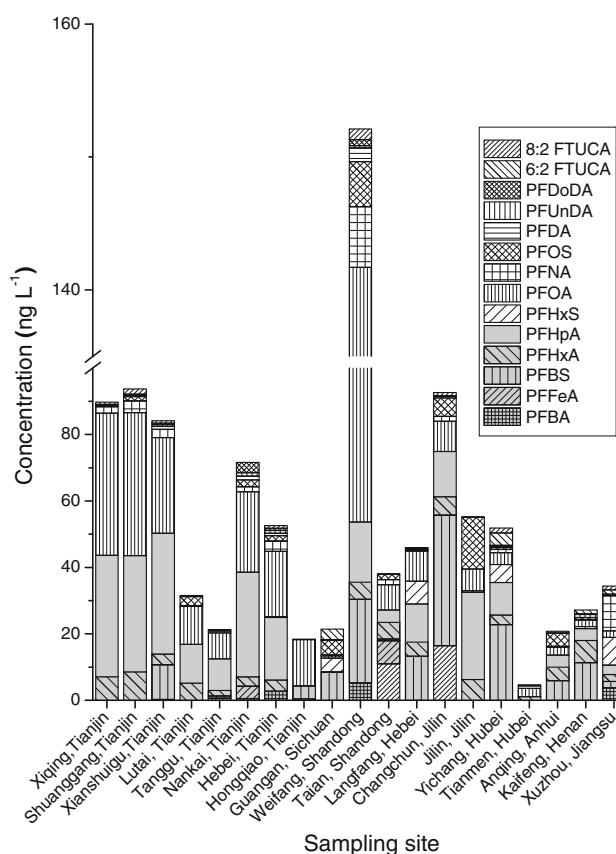
Fig. 2 Concentrations of individual PFC analytes in precipitation samples from different sampling sites of the east and central China in February 2010

frequency and concentration of PFOA, PFOS could not be detected at seven sampling sites; its concentrations were approximately 1 order of magnitude less than those of PFOA (range 0.6–15.6 ng L^{-1}), which contributed to 0.7–19.2 % of the total PFC concentration. The ratio of PFOA and PFOS was calculated for precipitation samples at the four sampling sites in Tianjin, where both PFOA and PFOS were detected, and the ratio ranged from 4.1 to 33.3 (mean 15.4). Kwok et al. (2010) reported the flux of individual PFCs in wet deposition in four cities from different countries around the world, and the ratio of PFOA to PFOS was in the range of 1.3–8.2. Kim and Kannan (2007) studied PFC distribution in rain water ($n = 11$) and snow ($n = 21$) from Albany, and the results showed the ratio of PFOA to PFOS in rain water and snow were 7.0 and 7.9, respectively. The greater ratio of PFOA and PFOS in Tianjin, compared with the data in the literature, may indicate more severe pollution of PFOA and its possible precursors in the atmosphere in Tianjin. Moreover, comparison of the ratio of PFOA and PFOS was performed between precipitation samples and surface water samples in a neighboring river. Haihe River is a main river flowing through the city of Tianjin, and the sampling sites for the

precipitation samples were all near Haihe River. In our former study (Li et al. 2011), we investigated PFC concentrations in water phase and the corresponding sediment at 16 sampling sites in Haihe River. Based on the average concentrations from these 16 sites, the ratios of PFOA to PFOS were calculated to be 4.1 and 0.3 for water and sediment, respectively. The ratio of PFOA and PFOS in precipitation is obviously greater than that in Haihe River; hence, it is likely that other sources, such as discharge of wastewater-treatment plants, might exist for the PFOS in Haihe River in addition to precipitation. We found that the concentration of PFOS increased significantly in a sewage canal after it received the discharge of the effluents of wastewater-treatment plants (Li et al. 2011). However, Haihe River is a reserved drinking water resource, and thus because any discharge of wastewaters is prohibited, and we did find clear spatial distribution of PFOS along Haihe River. Hence, the PFOS in surface water of Haihe River may have other non-point sources. In addition, the greater vapor pressure of PFOA (9.2×10^{-8} atm, 20 °C), compared with that of PFOS (3.3×10^{-9} atm, 20 °C) (Vecitis et al. 2008), might play an important role in this phenomenon. The results are consistent with previous precipitation monitoring in the areas of Tsukuba, Kawaguchi, and Tokoyo, Japan; Slingerlands and Albany, United States; Patna, India; and Toulouse, France (Kwok et al. 2010).

PFHpA was detected in the samples from 17 sites, except Yichang, Hubei province, and Hongqiao district, Tianjin, at concentration ranging from 2.8 to 36.5 ng L^{-1}. PFNA also had a relative high detection ratio of 9 of 19 sample sites, and the concentrations were between 0.8 and 10.5 ng L^{-1}. The PFHpA and PFNA might come from the oxidation of 6:2 FTOH and 8:2 FTOH in the atmosphere initiated by reaction with ·OH radicals (Ellis et al. 2004). Other short-chain PFCAs and PFASs, such as PFBA, PFPeA, PFBS, and PFHxS, were observed at low frequencies and low concentrations, with the detection ratio (concentration range) being 42.9 % (0.1–14.5 ng L^{-1}), 14.3 % (0.8–7.0 ng L^{-1}), 38.1 % (1.2–25.2 ng L^{-1}), and 57.1 % (0.2–8.6 ng L^{-1}), respectively. The long-chain (C > 9) PFCAs were seldom detected, and the concentrations were low (<2.0 ng L^{-1}). A previous study of PFCs in rain water samples from two cities in Japan also showed low concentrations of long-chain PFCAs and PFASs (Taniyasu et al. 2008).

Few reports are available on the occurrence of 6:2 and 8:2 FTUCA in atmosphere and wet precipitation (Taniyasu et al. 2008). In the present study, 6:2 FTUCA was detected at three sampling sites at concentrations of 3.7 ng L^{-1} at Yichang, Hubei province; 3.2 ng L^{-1} at Guangan, Sichuan province; and 1.3 ng L^{-1} at Kaifeng, Henan province. 8:2 FTUCA was detected at eight sampling sites, but the concentrations were all below the LOQ. The reason for the

relatively low detection frequencies and concentrations of 6:2 FTUCA and 8:2 FTUCA in the precipitation samples might result from the fact that they are unstable intermediates from FTOH atmospheric degradation and break down quickly (Ellis et al. 2004). x:3 acids, the relatively stable transformation products from 6:2 FTOH and 8:2 FTOH aerobic biodegradation (Wang et al. 2009; Liu et al. 2010b), were not detected in all of the samples. This confirms the previous discussion that biodegradation and photodegradation of FTOH follow different pathways. x:3 acids may be generated in terrestrial and aquatic systems, and they are unlikely to enter into the atmosphere due to their high solubility and low vapor pressure. The water solubility of 5:3 and 7:3 acids are 44 g L^{-1} (SciFinder, CAS: 914637-49-3) and 3 mg L^{-1} (pH 7, 25 °C) (SciFinder, CAS: 812-70-4), respectively, being greater than the corresponding PFCAs and PFASs with the same carbon length. Meanwhile, the vapor pressures of 5:3 and 7:3 acids are not high, being 19.6 Pa (SciFinder [CAS 914637-49-3]) and 3.2 Pa (SciFinder [CAS 812-70-4]), respectively, comparable with that of PFOA (4.1 Pa at 25 °C, USEPA 2009). Moreover, the concentrations of 5:3 and 7:3 acids in the aquatic system are low due to the fact that their precursors, FTOHs, are more likely to exist in atmosphere.

Several derivatives of FOSA used to be extensively applied as surfactants. Once these compounds are released to the atmosphere, they underwent atmospheric degradation to form PFOS (Ahrens et al. 2011). Hence, several potential precursors of PFOS, including FOSA n-Me-FOSA n-Et-FOSA n-Me-FOSAA, and n-Et-FOSAA, were measured in this study, and none of these precursors was detected in the collected samples. Their non-detection is consistent with the low frequency and concentration of PFOS in the precipitation samples in this study.

PFCA and PFAS Seasonal Trends in Precipitation in Tianjin

To determine the seasonal variations of PFCs in concentration and homologue distribution pattern in precipitation, samples from nine precipitation events at the sampling site in Nankai district, Tianjin were collected during a half year on January 2, February 8 and 22, May 3 and 16, June 9 and 18, and July 1 and 9, 2010, respectively. The detail meteorological condition of sample collecting and the characteristics of the water phase are listed in Table SM 4. Figure 3 shows the seasonal variation trend of individual and total PFCs in these precipitation samples.

The highest concentration of total PFCs (147 ng L^{-1}) was detected in the precipitation event on June 9, 2010. The total PFC concentrations in precipitation on January 2, May 16, and February 8 were also relatively high: 77.3,
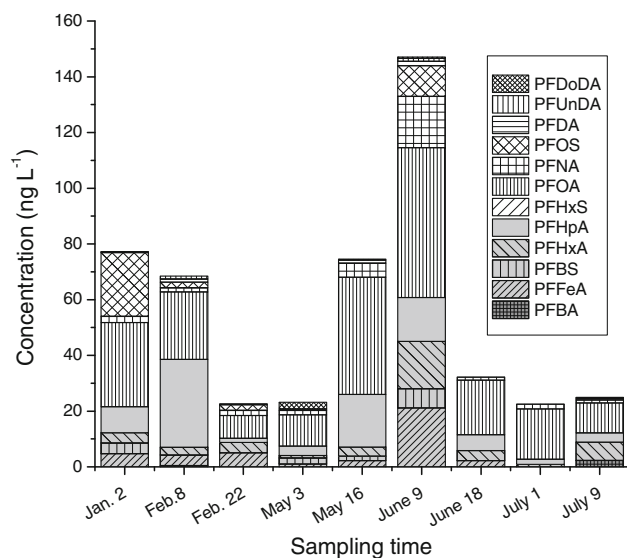
Fig. 3 Seasonal variation of concentrations of total and individual PFCs in the precipitation samples from the sampling site of Nankai district, Tianjin, China, during half a year in 2010

Fig. 4 Time trend of PFCs during one precipitation event at the sampling site of Nankai district, Tianjin, China, on June 18, 2010

74.6, and 68.5 ng L^{-1}, respectively. The target PFCs in the remaining five precipitation events were relatively low: 22.5–32.2 ng L^{-1}. No obvious seasonal variation trend was observed for the total PFCs in the designed sampling time. To assess seasonal variation, the average concentrations of total PFCs based on the season were calculated. The average total PFC concentration in the winter was the highest, 72.9 ng L^{-1}, and the lowest occurred in the spring, 22.9 ng L^{-1}. A relatively high average concentration of total PFCs (60.3 ng L^{-1}) was detected in the summer. The high PFC concentration in winter could be ascribed to the heavier air pollution that usually occurs in north China, whereas the relatively high PFC concentration in summer might be due to the fact that the high temperature accelerates the volatilization of PFCs or their volatile precursors, thus resulting in high PFC concentrations in the atmosphere. Kwok et al. (2010) observed the seasonal change of PFCs in precipitation in the northeastern United States and Japan during the course of 3 years, and both sampling sites showed no clear seasonal trend. Moreover, the scavenging efficiency of snow is considered to be relatively high compared with rain (Murray and Andren 1992; Lei and Wania 2004) due to its longer residual time in the atmosphere. However, no obvious difference in PFC concentrations in snow and rain was found in this study. The average concentration of total PFCs during in the three snowfall events was 56.1 ng L^{-1} compared with 54.1 ng L^{-1} during the six rain events.

PFHxA, PFHpA, PFOA and PFNA were detected in all of the nine precipitation samples in Tianjin at concentration ranges of 0.8–6.5, 1.9–31.5, 8.2–53.8, and 0.8–18.5 ng L^{-1}, respectively. PFPeA was recorded in six of nine samples at
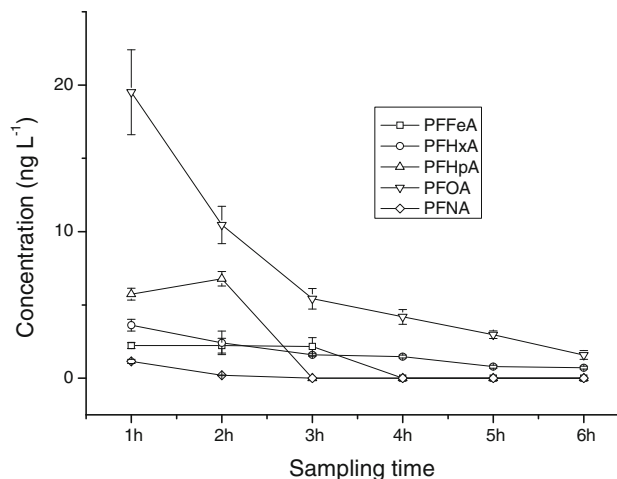
concentrations ranging from 1.1 to 21.2 ng L^{-1}. PFBS and PFDA had the same detected ratio of 44.4 % (four of nine events), and their concentration ranges were 1.2–6.9 and 1.1–1.6 ng L^{-1}, respectively. PFBA and PFUnDA were only detected in two precipitation samples. The concentrations of PFBA were 0.5 and 2.4 ng L^{-1}, whereas the concentrations of PFUnDA were below LOQ (Table SM 3). PFOS was detected in five samples at a concentration range of 0.2–22.8 ng L^{-1}. The rest of the analytes were not detected in all of the nine samples collected from Nankai district sampling site during a half year.

The concentrations of different PFC homologues did not change synchronously over the time. The highest concentration of PFPeA, PFBS, PFHxA, PFOA, PFNA, PFDA, and PFUnDA occurred on June 9, 2010, and PFOA was the dominant PFC in this precipitation event at a concentration of 18.1 ng L^{-1}. PFHpA in the precipitation event on February 8, 2010, was less than at other sampling times. The highest concentration of PFOS was detected in the event of January 2, 2010. No significant seasonal variation trend was shown for each PFC homologue. Many factors could have influenced the concentration variation trend, including precipitation amount, frequency, temperature, wind direction, wind velocity, original atmospheric concentrations of PFCs, etc. Among these factors, temperature and atmospheric concentration of PFCs are more important in determining the concentration of PFCs in the precipitation samples.

PFCA Time Trend from One Precipitation Event

Six successive precipitation samples were collected every hour during a precipitation event on June 18, 2010, at the sampling site of Nankai, Tianjin. All of the detected PFCs showed a descending trend over time during the event

(Fig. 4). The time trend of PFCs in this study was similar with the those of previous studies conducted in the cities of Kawaguchi, (Taniyasu et al. 2008), Tsukuba, and Kawaguchi, Japan, and Albany, United States (Kwok et al. 2010).

PFHxA and PFOA were detected during the entire 6-hour precipitation event at concentration ranges of 0.7–3.6 and 1.6–19.5 ng L^{-1}, respectively. The concentration of PFOA was the highest in the first sample at 0–1 h (19.5 ng L^{-1}) and decreased markedly, whereas the concentration of PFHxA was relatively low during the initial 1st h (3.6 ng L^{-1}) and decreased at a relatively low rate. The highest concentration of PFHpA, 6.8 ng L^{-1}, occurred in the second sample at 1–2 h, and afterward its concentration decreased rapidly to below LOQ. The concentrations of PFPeA and PFNA were low, and they were detectable only during the initial 3 (0.2–2.2 ng L^{-1}) and 2 h (0.8–1.2 ng L^{-1}) hours, respectively.

Generally, all of the detected PFCAs (C5 through C9) showed greater concentrations at the initial period of precipitation events and then decreased over time during the precipitation. This is consistent with the idea that initial wet deposition can scavenge substantial PFCAs from the atmosphere (Young et al. 2007). This high removal rate may also have benefited from the neutral pH (7.2, Table SM 4) of the precipitation, which is greater then the pKa of the predominant PFCs (e.g., the pKa of PFOA is 3.8 ± 0.1). Hence, the PFCs existed mainly as anions and could be readily dissolved into the precipitation by way of in- and below-cloud scavenging (Kwok et al. 2010).

Contrary to the present study, the concentration of PFOS was found to fluctuate during a snow event in Shenyang, China, in 2006, whereas PFOA concentrations remained nearly constant during the snow event (Liu et al. 2009b).

This might have resulted from the PFCs concentration that existed in the atmosphere and multiple meteorological and geographical conditions affecting the scavenging efficiency as mentioned previously.

PFCAs and PFASs in Surface Runoff

Before entering into surface water, precipitation would contact with the dust or the suspended soil particle on the earth surface. Contaminant residues on the earth's surface as dust or particulate matter thereon may enter precipitation samples. Hence, surface runoffs are usually more heavily polluted than the precipitation (Bucheli et al. 1998; Watts et al. 2010). Surface runoff has been considered to be s a main source of PFCs for surface water (Kim and Kannan 2007; Murakami et al. 2009; Nguyen et al. 2011). Zushi et al. (2008) reported that PFC concentrations in surface runoff along Tsurumi River basin, Japan, were 1.3–8.5 times greater than those in the river.

Three sites with different characteristics—a university campus, a gas station, and a primary highway—were selected as sampling sites to conduct a primary investigation of PFC contamination in surface runoff (Fig. 5). Only PFHxA, PFHpA, PFOA, and PFNA were detected in original precipitation samples from July 1, 2010, and the contents of the rest analytes were below the LOQ of the analytical method. The predominant PFC in the precipitation was PFOA at the concentration of 18.1 ng L^{-1}, accounting for >80 % of the total PFCs of precipitation event on July 1, 2010. PFNA also had a high concentration, 2.0 ng L^{-1}. The concentration of PFHxA and PFHpA were 0.8 and 1.9 ng L^{-1}, respectively. The concentrations of PFOA in the three types of surface runoff were greater then

Fig. 5 Comparison of PFC concentrations in surface runoffs of different characteristics and the corresponding precipitation
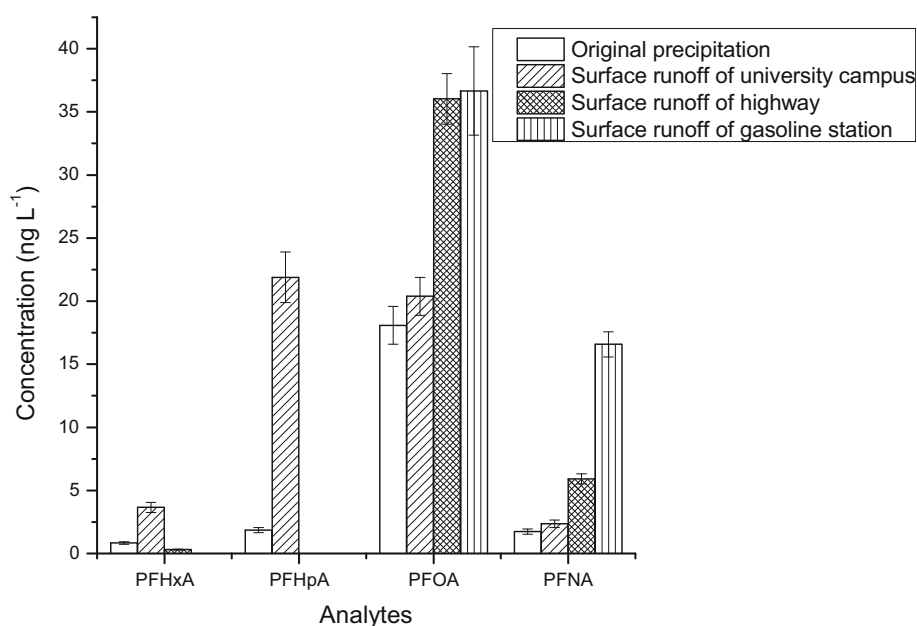
those in the original precipitation (Fig. 5). This result is consistent with the investigation of PFCs in surface runoff in Albany, United States, by Kim and Kannan (2007). Augmentation factors (the ratio of PFC concentration in surface runoff to that in original precipitation) for PFOA decreased in the following order: gas station (2.0) > highway (1.9) > university campus (1.1). PFNA had the similar trend in the three kinds of surface runoff with PFOA but with greater augmentation factors: gasoline station (9.5) > highway (3.4) > university campus (1.4). The presence of coal tar sealant at the gasoline station and highway sites might have increased the mass of PFCs in runoff water. Concentrations of PFHxA and PFHpA in the surface runoff at campus were also greater compared with their concentrations in the original precipitation samples: The augmentation factors were 4.4 and 11.8, respectively. It is not clear why PFHxA and PFHpA were not observed (below LOD) in surface runoff at the highway and gas station sites. They might have been sorbed to land surface or solid (Zushi and Masunaga 2011). To determine the effect of human activity on PFC contamination in runoff, more samples of different types of precipitation events, as well as the simultaneous measurement of both the precipitation and the dust before and after the precipitation, should be studied in future.

Conclusion

Large-scale sampling across eastern and central China elucidated the extensive PFC concentrations in precipitation in China. PFCs in particulate matters separated from the precipitation could not be detected, partially due to the low mass of the particulate matter. PFOA had the highest concentration and detection frequency in water phase of the precipitation. Many meteorological parameters may affect PFCs in precipitation, which led to the fact that no obvious seasonal variation trend was observed in both individual and total PFCs. The descending concentration trend in consecutive samples in one precipitation event could testify to the precipitation's PFC removal mechanism. The target analytes in runoff samples collected from different sites did not show a consistent trend, with individual PFC increasing in some cases but decreasing in others.

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