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Neutral and ionic per- and polyfluoroalkyl substances (PFASs) in atmospheric and dry deposition samples over a source region (Tianjin, China)☆

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ABSTRACT

Per- and polyfluoroalkyl substances (PFASs) were detected in the atmosphere of a source region in Tianjin, China. Fluorotelomer alcohols (FTOHs) were the dominant neutral PFASs in the atmosphere with total concentrations of 93.6-131 pg/m^3 and 8:2 FTOH contributing the most, whereas perfluorooctane sulfonamide derivatives (PFOSAs) were two magnitudes lower or undetected. In comparison, ionic PFASs (perfluoroalkyl carboxyl acids (PFCAs)) in the atmosphere were detected at similar or even higher levels. At wastewater treatment plants (WWTPs), the air over influent was found with higher levels of FTOHs than over aeration tank and effluent; whereas in the air over the aeration tank, the concentrations of PFOSAs and nonvolatile ionic PFASs substantially increased, suggesting a possible direct release of ionic PFASs to the atmosphere besides the atmospheric conversion from volatile precursors. In the air phase, a low proportion (1-5%) of PFCAs was subjected to dry deposition in the source region. Interestingly, the dry-deposition-to-bulk-air ratios of PFCA analogues were the lowest at medium chain lengths (C8 and C9) and increased with either shorter or longer chain length. The extraordinary affinity of shorter-chain PFCAs (C6-C7) to particles was presumed to be due to their smaller molecular size favoring the interactions between the carboxyl head groups and specific sorption sites on particulate matter.

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) have been produced and applied in manufacturing a variety of commercial and industrial products (Kissa, 2001). After the phasing-out of long-chain (C8 and C10) perfluoroalkane sulfonyl fluoride (PASF)-based products, the demand for fluorotelomer alcohol (FTOH)-based products has been increasing annually (Wang et al., 2014a). Meanwhile, a perfluorooctanoic acid (PFOA) Stewardship Program was implemented in 2006 to eliminate long-chain PFCAs in products by 2015 (US-EPA, 2010). Even so, both PASF-based and FTOH-based chemistries have rehabilitated in countries without rigid regulation on long-chain PFASs in continental Asia (Wang et al., 2014a). Particularly in China, accommodating emerging manufacturers as well as consuming a substantial amount of PFAS products, emission profiles of PFASs should be even more complicated.

Neutral PFASs such as FTOHs are recognized as volatile precursors that may give rise to gas-phase PFCAs via OH-initiated degradation (Ellis et al., 2004). The long range atmospheric transport (LRAT) of FTOHs and their subsequent degradation are believed to be a dominant source of PFCAs detected in remote environments (Ellis et al., 2004). Although data are rather scarce, neutral PFASs especially FTOHs were found to be dominant contaminants in the atmosphere around the world, with a concentration range of 0.3–1516 pg/m^3 (Dreyer et al., 2009; Müller et al., 2012). PFASs have been reported to occur in the atmosphere at substantial levels of 0.2–498 pg/m^3 in mainland China (Li et al., 2011b). Meanwhile, high concentrations of PFCAs in precipitation have been reported worldwide adjacent to urban areas (Kwok et al., 2010; Zhao et al., 2013b), for which incomplete degradation from precursors was also considered as a main source (Styler et al., 2013). However, the occurrence of both the neutral and ionic PFASs in the

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atmosphere from a source region with dense population and heavy industry has not been well accounted for.

In source regions, wastewater treatment plants (WWTPs) have been suggested to contribute to the burden of PFASs in the atmosphere, especially for the volatile neutral PFASs (Ahrens et al., 2011). Additionally, treatment processes at WWTPs may also give rise to ionic PFASs due to the incomplete degradation of the neutral precursors during the treatment process (Zhang et al., 2013b; Zhao et al., 2013a). However, the direct emission of PFASs from WWTPs to the atmosphere has not been clarified.

The migration of atmospheric chemicals can be significantly influenced by their partitioning between gas and particle phases, and hence being an important aspect to evaluate for the LRAT potential. A long-term monitoring study on an urban area demonstrated that neutral PFASs primarily occurred in gas phase (Wang et al., 2014b). The occurrence of ionic PFASs in the atmosphere is less clear. More Recently, ionic PFASs have been found to preferentially occur in the finest atmospheric particles such as aerosol, which is able to undergo atmospheric transport (Dreyer et al., 2014).

Studies on Tianjin City and its ancillary areas have showed pronounced levels of ionic PFASs in surface waters, WWTPs, as well as in precipitation and surface runoff (Li et al., 2011a; Yao et al., 2014; Zhao et al., 2013b). Therefore, Tianjin City could be qualified as a typical source region of PFASs, of which the profiles in the atmosphere is still unknown. In the present study, the atmospheric concentrations of both neutral and ionic PFASs were investigated from urban to rural areas and the air concentrations over different stages of WWTPs were compared. In addition, PFAS concentrations in dry deposition samples from typical sampling sites were also measured and their relations with the corresponding air samples were discussed.

2. Materials and methods

2.1. Preparation and sampling campaigns

Sorbent-impregnated polyurethane foam (SIP) disk-based passive air samplers, which have been specifically developed to obtain a higher sampling capacity for PFASs and widely used in air sampling campaigns (Ahrens et al., 2011; Genualdi et al., 2010; Li et al., 2011b), were used in the present study. Before assembling, the polyurethane foam (PUF, Tisch Environmental, Cleves, OH) disks were prepared according to the previously proposed method (Shoeib et al., 2008). Briefly, the PUF disks were precleaned by soaking in Milli-Q water and Soxhlet extracting with acetone and petroleum ether successively each for 24 h. Amberlite XAD-4 (Supleco, Bellofonte, PA) was precleaned by ultrasonication with methanol, dichloromethane and hexane in a row each for 30 min before being ground to powder in a Retch planetary ball mill with particle size of approximately 0.75 μm. The powder was further cleaned by Soxhlet extractions using methanol, dichloromethane and hexane for 24 h in total. Before coating, both PUF disks and XAD-4 powder were dried in vacuum desiccators. By being dipped in a slurry of XAD-4 in hexane and dried under vacuum, a PUF disk was well impregnated with XAD-4 powder. The finished SIP disks were wrapped up with aluminum foil and sealed in polypropylene (PP) bags individually, and stored at −20 °C until deployment. All metal accessories of the samplers were prerinsed with Milli-Q water and further rinsed or ultrasonicated with methanol three times in the laboratory, and air dried before being sealed up in PP bags. All passive samplers were assembled and loaded with SIP disks on site immediately before the deployment to avoid contamination in transit.

The deployment sites can be characterized into two collections: 5 samplers were deployed according to geographic and urban features to include urban, suburban, rural and background sites; the other 6 samplers were deployed at two WWTPs where air about 1 m above the surface of influent (before grid), aeration tank and effluent (secondary sedimentary tank) was sampled, respectively. The two WWTPs are over 50 km apart and function for different areas. Sites other than WWTPs were selected with caution to keep away from main roads to avoid heavy traffic. The geographic map of the sampling campaign is shown in Fig. S1 and the detailed information is given in Table S1 (Supporting information, SI). The sampling campaign started between 26th June and 1st July 2013 and lasted for 90 days for each site. Within the period of deployment, the predominant wind direction was south or southeast with a speed of 12–19 km/h or lower and the temperature varied between 16 and 37 °C. After sampling, all the samplers were dissembled on site and the SIP disks were retrieved and sealed in their original foils and PP bags. All disks were kept at −20 °C before extraction.

Dry deposition were sampled at three locations of the city center site, the rural site and WWTP 2 simultaneously using a pre-cleaned stainless steel cylinder bucket (50 cm in diameter × 80 cm in height). The collection lasted for 30 days in early 2013 when no wet deposition occurred. At the end of the sampling campaign, particulate matter in each bucket was carefully collected and transferred into a PP tube, which was kept at −20 °C before extraction.

2.2. Pretreatment of the samples

The SIP disks were Soxhlet-extracted with ethyl acetate (E1) and methanol (E2) each for 24 h, successively. Before extraction, 5 ng of each mass-labeled standard was added. Both E1 and E2 extracts were concentrated to less than 5 mL via rotary evaporation, respectively. The concentrates were then transferred to PP tubes. They were further dehydrated with anhydrous sodium sulfate and concentrated to 500 μL under a gentle stream of pure nitrogen. Twenty-five milligrams of dispersive EnviCarb (120/400 mesh, CNW Technologies, GmbH, Düsseldorf, Germany) was added to the final concentrate. After gently shaken for 5 min, the EnviCarb was removed by centrifugation at 15,000 g for 10 min. The supernatant was to be analyzed. A 100-μL aliquot of E1 was transferred into an autosampler vial to be analyzed for neutral PFASs. Another 100-μL aliquot of E1 was evaporated to dryness under pure nitrogen stream in an autosampler vial and redissolved with 100-μL aliquot of E2, and this combination was analyzed for ionic PFASs.

Repeated ultrasonic extraction with methanol (Fraser et al., 2013) was used for the dry deposition samples with modifications. Prior to extraction, 5 ng of each mass-labeled internal standard of PFASs was spiked in approximately 500 mg of each sieved sample (<150 μm). The sample was then extracted in 5 mL methanol under sonication for 30 min. After centrifugation at 3500 g, the supernatant was collected. A second aliquot of 5 mL methanol was added to repeat the procedure and was combined with first extract after centrifugation. The combined extract was further reduced to a volume of 500 μL by evaporation under a gentle stream of nitrogen. The concentrate was cleaned by being gently shaken with 25 mg dispersive EnviCarb and then centrifuged at 15,000 g for 10 min. A 100-μL aliquot of the supernatant was transferred into an autosampler vial before analysis.

2.3. Instrumental analysis

A total 16 PFASs were measured for the samples. The information on all the suppliers of the external standards and labeled internal standards used for instrumental analysis and solvents used for extraction is listed in the SI.

The neutral PFASs (3 FTOHs, 2 FOSEs and 2 FOSAs) were