

OCCURRENCE AND DISTRIBUTION OF PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES (PFASs) IN MULTI-ENVIRONMENTAL MATRICES AROUND TWO FLUORO-CHEMICAL MANUFACTURING PARKS IN FUXIN, CHINA

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Introduction

As a class of good-quality surfactant, perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been widely used in numerous industrial and household products such as textile finishing agents, leather treatment agents, coatings, and pesticides [1,2]. Due to their wide use, PFASs, including ionic perfluoroalkyl sulfonic acids (PFSA) and carboxylic acids (PFCA) and neutral fluorotelomer alcohols (FTOHs) and fluorotelomer iodides (FTIs), have been detected in various environmental media, including air, water, soils, dusts, sediments, wildlife and human beings [3-7]. Due to the ubiquitous occurrence, along with the persistence, global and national legislations have been established to control the manufacture and use of long-chain PFASs ($C \geq 6$), especially C8-PFASs and some long-chain PFASs were gradually replaced by short-chain (C4-C7) congeners [8,9]. However, the manufacture of C8 substances had shifted to China [10].

Multiple processes have been involved in the distribution and fate of PFASs, and many of processes are still poorly understand. It has been revealed that once released in the environment, fluorotelomer-based precursors (e.g., FTOHs and FTIs) can be degraded to metabolites including PFCA via (photo)chemical and biological degradations [11-13], which is recognized an important source of ionic PFASs in the environment. Besides, the transport way of PFASs is still unclear, and it was recently found that outdoor dusts play an important role in the global transportation of ionic PFASs (i-PFASs) [7].

Since 2004, two fluorochemical manufacturing parks (FMPs) have been developed in Fuxin, which makes the city as a fluorine industrial centre in China [14]. Both electrochemical fluorination and telomerization were implied to produce PFASs products. Previous studies reported that short-chain PFAAs were the predominant PFASs in FMPs [14-16]. In this study, multiple environmental matrices, including air, precipitation, surface river water, shallow underground water, outdoor dust, soil, river and reservoir sediment and leaves were taken around the two FMPs. The objectives were to investigate the occurrence and distribution of PFASs in multi-environmental matrices around two FMPs, to discuss the transportation of PFASs via air and water, to make comprehensive understanding of the PFASs fate around the two FMPs, and to evaluate the potential exposure risks to local inhabitants.

Materials and methods

Air (n=8), precipitation (n=3), surface river water (n=15), surface reservoir water (n=2), shallow underground water (n=4), outdoor dust (n=12), soil (n=21), surface river and reservoir sediment (n=13), leaves of the willow (*Salix babylonica*, n=7), leaves of the maize (*Zea mays*, n=7), and needles of pyramidalis (*Sabina chinensis*, n=2) samples were collected from the ambient environment around two FMPs in Fuxin, China in September and

October 2016. Air samples were collected using passive air samplers employed sorbent-impregnated polyurethane foam (SIP) disks. The SIP disk samplers were deployed from 1st September to 15th October 2016 (45 days). Precipitation samples were collected using stainless steel basin and stored in 500 mL PP bottles. Shallow underground water samples were collected from the hand pressed well and stored in 500 mL PP bottles. Surface water samples were collected from river and reservoir using a 5 L organic glass hydrophore and then stored in 500 mL PP bottles. At the same time, surface river and reservoir sediment samples (about 0-5 cm deep) were collected using a grab sampler and stored in 500 mL PP bottles. At each sampling site, outdoor dust samples were collected from out wall surface of a building 1 m above the ground using a disposable wool brush and a polypropylene (PP) tube. Surface soil samples (0-5 cm) were collected with a stainless steel trowel and sealed in polyethylene bags. Leaves were collected using stainless steel scissors, wrapped in aluminium foil and stored in polyethylene bags. All sampling tools were precleaned with MeOH and Milli-Q water.

After being spiked with mass-labelled internal standards (10 μL of 500 $\text{pg}/\mu\text{L}$; containing mass-labelled 8:2 fluorotelomer unsaturated carboxylic acid (8:2 FTUCA), PFASs, PFCAs, FTOHs, perfluorooctane sulfonamides (FOSAs) and perfluorooctane sulfonamidoethanols (FOSEs)) and the SIP disks were Soxhlet extracted by ethyl acetate (S1) and methanol (S2) each for 24 h, successively. The extracts were concentrated by rotary evaporation followed by gentle nitrogen blow down to 0.5 mL and cleaned up by EnviCarb (50 mg, 100-400 mesh, Supelco, USA). A 100- μL aliquot of S1 was analysed for neutral PFASs (n-PFASs). Another 100- μL aliquot of S1 was evaporated to dryness by gentle nitrogen and dissolved with 100- μL aliquot of S2, and this combination was analyzed for i-PFASs [17]. After being spiked with mass-labelled internal standards (10 μL of 500 $\text{pg}/\mu\text{L}$; containing mass-labelled 8:2 FTUCA, PFASs and PFCAs), the water samples were solid phase extracted (SPE) using Oasis weak anion exchange (WAX) cartridges (6cc, 500 mg, Waters, USA). After being spiked with mass-labelled internal standards (10 μL of 500 $\text{pg}/\mu\text{L}$; containing mass-labelled 8:2 FTUCA, PFASs, PFCAs, FTOHs, FOSAs and FOSEs) and the outdoor dust, soil, sediment and leaves were sonicated using methanol [18]. The analytical quantification of the samples was done using gas chromatography mass spectrometry (GC-MS; Agilent Technologies GC 7890A series coupled to 5975C Triple-Axis detector, Palo Alto, CA, USA) for n-PFASs and high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS; Agilent Technologies LC 1260 series coupled to 6460 Triple Quad system, Palo Alto, CA, USA) for i-PFASs.

Results and discussion

FTOHs and FTIs were the predominant n-PFASs in air with the sum concentrations ranging from 122 to 7870 pg/m^3 and 4.48 to 922 pg/m^3 (Figure 1a), respectively. Perfluorobutanoic acid (PFBA), perfluorobutane sulfonate (PFBS) and perfluorooctanoic acid (PFOA) were the predominant i-PFASs in air (Figure 1b), surface river water (Figure 1c), surface reservoir water (Figure 1c), shallow underground water (Figure 1c), outdoor dust and sediment. PFBA (0.228-131 ng/g) and perfluoroheptanoic acid (PFHpA) (0.0293-135 ng/g) were the predominant i-PFASs in soil. PFBA was the predominant PFASs in leaves from Fuxin (50.5-99.5%). Downstream of the effluent from the FMPs, PFBA and PFBS concentrations up to 11900 and 5810 ng/L were detected in the River Xi. Short-chain i-PFASs (C4-C7) predominated in the surface river water (14.8-98.7%), while long-chain PFASs (C8-C12) prevailed in the surface sediment. Field-based sediment-water distribution coefficients of PFCAs increase linearly ($R^2=0.99$, $p<0.01$) with the chain length increasing from C4 to C12, while decreased from C2 to C4. Trifluoroacetic acid (TFA) were detected in all environmental matrices. TFA concentrations were 1 or 2 orders of magnitude higher than other individual i-PFASs in most samples. The levels of PFASs in surface river water, air (Figure 2), and outdoor dust decreased exponentially with increasing distance from the FMPs (significantly in the

first 5 km), thus, FMPs were the point sources in the studying area. Concentrations of 8:2 FTUCA in air and outdoor dust significantly correlated with those of long-chain PFCAs (C9-C12) and 8:2 FTOHs, suggesting the degradation of precursors (e.g., FTOHs and FTIs). For residents around the two FMPs, potential health risks existed, due to high concentrations of PFASs in air, outdoor dust, water and soil. Adults around the FMPs were exposed to 2.73×10^{-3} -0.177 ng/kg/d of FTOHs and 5.97×10^{-3} -0.143 ng/kg/d of PFOA through air inhalation, which were significant higher than those via dust and soil ingestion.

Acknowledgements

This study was financed by the National Natural Science Foundation of China (Nos. 41573097; 41603101).

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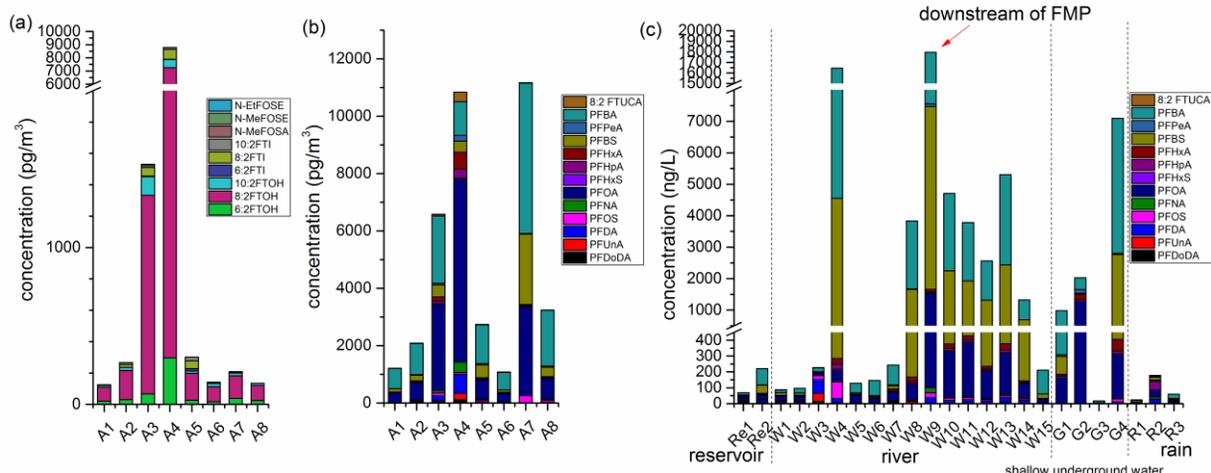


Fig.1. Levels of (a) neutral and (b) ionic PFASs in the air samples and (c) water samples collected around two fluorochemical manufacturing parks, Fuxin, China.

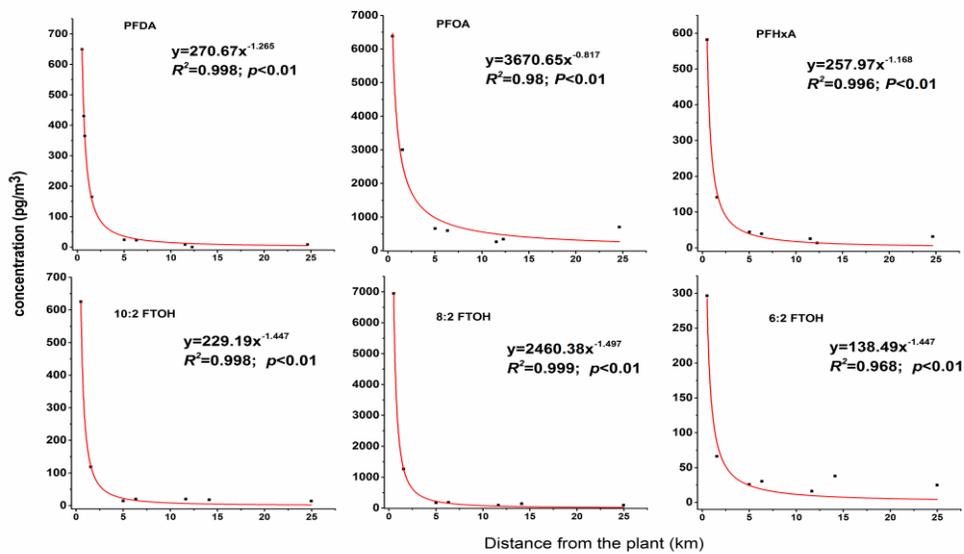


Fig.2. Decline of PFASs concentrations in air with the distance from the fluorochemical manufacturing parks, Fuxin, China.