



Concentration profiles and spatial distribution of perfluoroalkyl substances in an industrial center with condensed fluorochemical facilities



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HIGHLIGHTS

- PFOA and short-chain PFCAs were predominant in all the environmental samples.
- The center was a potential source of short-chain PFASs in the surrounding environment.
- The \sum PFASs in suspended particulate matter were much lower than those in dissolved phase.
- The sediment-derived $\log K_{oc}$ of PFOA was one log unit lower than the SPM-derived one.
- The spatial distribution of PFASs in tree leaves indicated airborne transport from the facilities.

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ABSTRACT

Jiangsu Hi-tech Fluorochemical Industry Park, China, is one of the largest fluorochemical industry centers in Asia and could be a point source of polyfluoroalkyl substances (PFASs) to the surrounding environment. Besides water, sediment and soil samples, tree leaves and bark were also collected to monitor airborne PFASs around the facilities. Perfluorooctanoic acid and short-chain perfluorocarboxylates including perfluorohexanoic acid and perfluoropentanoic acid were found predominantly in all the samples. The target \sum PFASs were distributed in the dissolved phase with a proportion of $96.5 \pm 2.9\%$. High concentrations of \sum PFASs (up to 12,700 ng/L in surface water) were found at sites near and within the wastewater treatment plant and the facilities. The \sum PFASs in the sediment/sludge were in the range of 3.33–324 ng/g dw. For the first time, tree samples were used for bio-monitoring airborne PFASs in the environment. The \sum PFASs in the tree leaf and bark samples were in the range of 10.0–276 and 6.76–120 ng/g dw, respectively. The spatial distribution of \sum PFASs in the tree leaves suggested that airborne PFASs could be transported from the center to the surrounding environment by prevailing wind.

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1. Introduction

Perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonates (PFASs), and other related perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been widely used in commercial products such as surfactants, textile, and aqueous fire-fighting foams, for several decades due to their outstanding thermal and chemical stabilities and hydro- and lipophobic properties (Buck et al., 2011). They are also used as additives or processing acids in industrial processes such as polymer manufacturing (EPA Denmark, 2013; Giesy et al., 2010; Post et al., 2012). They are ubiquitous in the environment and are even

found in remote regions such as the Arctic as a consequence of widespread usage. It is reported that long-chain PFCAs and PFASs could be bioaccumulated and biomagnified in food chains and may display adverse effects to animals and humans (EPA Denmark, 2013; Giesy et al., 2010). Thus, continuous concerns over their potential impacts on ecosystem and human health have led to regulatory actions against their production and application. For example, perfluorooctane sulfonate (PFOS) was listed as a new persistent organic pollutant by Stockholm Convention in 2009. Although a major PFAS manufacturer in the United States has phased-out the production of PFOS and related chemicals since 2002, the production has gradually increased in China since then (EPA US, 2012a; Xie et al., 2013; Lim et al., 2011).

Perfluorooctanoic acid (PFOA) is another PFAS compound which attracts lots of concerns due to its high production volume and high

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detection frequency in the environment. It has been considered as a potential human carcinogen by the US Environment Protection Agency (EPA) (EPA US, 2012a). Currently, eight major manufacturers in North America agreed with the US EPA to work toward eliminating emission of PFOA and related chemicals by 2015 (Vierke et al., 2012).

In China, due to the booming market and abundant resources of fluoride, the fluorochemical industry is one of the fastest growing industries. Several fluorochemical industry centers were founded in the past years, including Jiangsu Hi-tech Fluorochemical Industry Park. It was founded in 1999 and is one of the largest fluorochemical industrial centers in Asia. It has an area of 15.02 km² and is located in Jiangsu Province by Yangtze River in southeast China. There are more than twenty facilities manufacturing fluorine-based chemicals, including Arkema, DuPont, Daikin and Solvay in the center. The main products of these facilities are fluoropolymers such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF). Production of these fluoropolymers is the main source of PFOA and perfluorononanoic acid (PFNA) in the environment since they are used as processing acids during manufacturing (Dauchy et al., 2012; Dupont, 2012).

It was reported that PFASs with shorter fluorinated chain ($C_F < 7$) have less potential for bioaccumulation and lower toxicities (EPA Denmark, 2013). Therefore, along with the regulatory actions against long-chain PFASs, many manufactures have begun to produce and use PFASs with less fluorinated chain, such as perfluorohexanoic acid (PFHxA), as alternatives or additives of perfluorooctyl-based products (EPA US, 2012b; Dupont, 2013). Perfluorobutane sulfonate (PFBS) is produced as alternatives of PFOS and perfluorohexane sulfonate (PFHxS) as well (Zhou et al., 2013).

The large scale manufacturing of fluoropolymers in the center may result in the release of PFASs to the surrounding environment and finally threaten the ecological system (Dupont, 2012; Daikin, 2012). The C8 Health Project aimed to evaluate the adverse effects of PFOA on human health in Ohio and West Virginia communities contaminated by fluoropolymer production facility owned by DuPont (Hoffman et al., 2011; Shin et al., 2011). However, little is known about the impacts of the manufacturing activities in Jiangsu Hi-tech Fluorochemical Industry Park on the surrounding environment.

Vegetation can be used to indicate atmospheric contamination of volatile organic pollutants and has been used to identify pollution point sources (Simonich and Hites, 1995). It was reported that employing plant samples such as tree bark is an effective tool for monitoring atmospheric polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and other semi-volatile pollutants around emission sources (Rodriguez et al., 2012; Meredith and Hites, 1987; de Nicola et al., 2013). For PFASs, most of the studies focused on water, soil, sediment and aquatic organisms, while a few of studies using plants as a tool have been performed considering that they are less volatile.

To understand the contamination level of PFASs in the surrounding environment of Jiangsu Hi-tech Fluorochemical Industry Park, water and sediment samples were collected from the canals and ponds in or near the facilities. Besides, tree leaf and bark samples near the industrial facilities were also collected to investigate the possibility of using plants as biomonitoring tool for PFASs in atmosphere. Eleven PFASs were quantified in these samples. The results would provide useful information on the ecological risk assessment of PFASs in the surrounding environment due to the production activity of the industry facilities.

2. Materials and methods

2.1. Reagents and materials

The target PFAS analytes include the PFCAs with 4–11 perfluorinated carbons, and C₄, C₆, and C₈-PFASs. Perfluorobutane sulfonate (PFBS, 98%) and perfluorohexanoic acid (PFHxA, 98%) were obtained from Tokyo Chemical Industry Co., Ltd. (Japan). Perfluoropentanoic acid (PFPeA,

97%), perfluorododecanoic acid (PFDA, 96%) and perfluorododecanoic acid (PFDoA, 97%) were obtained from Acros Organics (Geel, Belgium). Perfluoroheptanoic acid (PFHpA, 98%), perfluorooctanoic acid (PFOA, 95%) and perfluorononanoic acid (PFNA, 97%) were purchased from Shanghai Adamas-Beta Reagent Co., Ltd. (Shanghai, China). Perfluorohexane sulfonate (PFHxS, 98%) was from Sigma-Aldrich (St. Louis, MO, USA). Perfluorododecanoic sulfonate (PFOS, 98%) was purchased from Kasei Kogyo Co., Ltd. (Tokyo, Japan). Perfluorodecanoic acid (PFUnDA, 96%) and the internal standards of perfluoro-1-(1,2,3,4-¹³C₄) octanesulfonate (¹³C₄-PFOS) and perfluoro-n-(1,2-¹³C₂) octanoic acid (¹³C₂-PFOA) were purchased from Wellington Laboratories (Guelph, Canada). HPLC-grade methanol (MeOH) was purchased from Concord Chemical Company (Tianjin, China). Mill-Q water was used.

2.2. Sample collection and storage

All samples were collected around the fluorochemistry industrial facilities in May, 2012 (Fig. 1). Water samples were collected at sites 1–17, 21, 23, 28 and 29 (totally 21 sites). Among those sites, site 8 was at a pond inside the wastewater treatment plant (WWTP) of the industrial center, sites 1–7 were located near the north part of the center and site 7 was at the drainage canal next to the WWTP, sites 9–13 were in Yangtze River near the south part of the center, sites 14–17 were at Wangyu River flowing into Yangtze River and sites 21, 23, 28 and 29 were along the No. 338 provincial road. Sediment samples were collected at sites 1–6 and site 23, while sediment was not available at other sites. One sludge sample was collected at site 8. Soil, leaves and tree bark samples were collected at sites 1, 2, 4, 7, 15–22 and 25–29 (totally 17 sites).

All fluorinated materials such as Teflon coated lab wares were avoided during sample collection, preparation and instrumental analysis to minimize contamination of the samples. Water samples were stored in 1.25 L polypropylene (PP) bottles and surface sediment and sludge samples were stored in PP plastic bags. The bottles and bags were pre-cleaned with MeOH and deionized water. Leaf and bark samples were collected from a typical and widespread local species, camphor, by cutting the leaves at 2 m high above the ground and the bark at height about 120–150 cm above the ground using stainless steel scissors, which were pre-cleaned with MeOH and deionized water. All the leaves contained petiole parts. At the same sampling sites, surface soil samples were collected simultaneously. All the samples were stored in pre-cleaned PP plastic bags. Upon back to laboratory, the leaf and bark samples were freeze-dried directly without washing and grounded. All the samples were then passed through a sieve (250 μm mesh size), and stored in plastic bags until extraction.

2.3. Sample pretreatment and extraction

One liter of water was filtered through a glass fiber filter (47 mm, pore diameter 0.7 μm, Whatman, pre-combusted at 450 °C for 5 h) to separate suspended particulate matter (SPM) from water. The dissolved phase was collected in a new PP bottle and extracted with solid phase Cleanert PEP cartridges (500 mg, 6 mL, Agela Technologies, Tianjin, China) as described in previous study (Zhao et al., 2012). The MeOH elute was concentrated to 1 mL under a nitrogen stream and transferred into an auto sampler vial. Five nanograms of internal standards of ¹³C₄-PFOS and ¹³C₂-PFOA was spiked before instrumental analysis. The SPM samples were extracted with 15 mL of MeOH by sonication for 20 min and then centrifuged (3000 rpm) for 10 min. This process was repeated once and the extracts were combined and diluted to 500 mL to pass through the Cleanert PEP cartridges, following the same procedure as described for the dissolved phase samples.

Five grams of dry soil or sediment and 10 mL of MeOH were added in a 50 mL PP tube. The mixture was vortexed to ensure complete mixing. Each tube was sonicated for 30 min and centrifuged at 3000 rpm for 5 min. The supernatant was transferred in a new PP tube. The procedure

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