



Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Tracing perfluoroalkyl substances (PFASs) in soils along the urbanizing coastal area of Bohai and Yellow Seas, China

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ARTICLE INFO

Article history:

Received 12 January 2018

Received in revised form

14 March 2018

Accepted 16 March 2018

Keywords:

PFASs

Sources

Life cycle analysis

Soil

Coastal area

ABSTRACT

With the shift of fluorine chemical industry from developed countries to China and increasing demand for fluorine chemical products, occurrence of perfluoroalkyl substances (PFASs) in production and application areas has attracted more attention. In this study, 153 soil samples were collected from 21 cities along the urbanizing coastal area of the Bohai and Yellow Seas. PFASs in this area were relatively higher, compared with other study areas. The concentrations ranged from 2.76 to 64.0 ng g⁻¹, and those in most sites were between 2.76 and 13.9 ng g⁻¹, with a predominance of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). Among the 21 coastal cities, contaminations of PFASs in Zibo, Nantong and Binzhou were elevated, which was likely affected by local fluorine chemical plants, equipment manufacturing and chemical industry, respectively. The total emissions of PFOA and PFOS were similar, with amount of 4431 kg and 4335 kg, respectively. Atmospheric deposition was the largest source, accounting for 93.2% of total PFOA and 69.6% of PFOS, respectively. In addition, due to application of aqueous film-forming foams (AFFFs) and sulfluramid, disposal of sewage sludge and stacking of solid waste, emission of PFOA and PFOS to soil was 1617 kg, accounting for 9.29% of the whole China. In general, pollution in Jiangsu, Shandong and Tianjin was more serious than those in Liaoning and Hebei, which was consistent with industrialization level and size of industrial sectors emitting PFASs.

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1. Introduction

Perfluoroalkyl substances (PFASs) are a class of anthropogenic surfactants possessing a perfluorinated moiety (C_nF_{2n+1}), which render PFASs thermally, chemically and biologically inert, making them “compounds of concern” for the environmental and biological effects (Loganathan et al., 2007; Taniyasu et al., 2015; Chen et al., 2017). PFASs have been widely used in both polymer applications, due to their hydrophobic and oleophobic properties, and surfactant applications, due to their unparalleled low aqueous surface tension since the 1950s (Loganathan, 2016; Wang et al., 2017). Currently,

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PFASs, particularly perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), are ubiquitous in the environment, even in remote areas, such as the Arctic (Armitage et al., 2009a; Zhao et al., 2012). However, because of their toxicological concerns on wildlife and humans, PFOA and PFOS have been subjected to a series of restrictions and regulations (Hekster et al., 2003; Kelly et al., 2009). PFOS, its salts, and its precursor, perfluorooctane sulfonyl fluoride (PFOSF), have been officially added to the list of the Stockholm Convention in 2009 (Wang et al., 2009). PFOA, its salts and related substances were listed in the European Union's regulation regarding the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) in 2017 (EU, 2017). Meanwhile, comments on the draft risk management evaluation on PFOA, its salts and related compounds were submitted to the Persistent Organic Pollutants Review Committee (POPRC), which has accelerated the management process of PFOA and related substances (POPRC, 2017).

PFASs can be emitted to soil via point sources (e.g. manufacture and processing sites, use of aqueous film-forming foams (AFFFs),

wastewater treatment plants, landfills) or diffuse sources (e.g. atmospheric deposition, runoff, use of sulfloramid) (Davis et al., 2007; Kim et al., 2014; Taniyasu et al., 2013), while PFASs in soils can be transported to the atmosphere, surface water and groundwater through volatilization, diffusion, leaching and runoff (Armitage et al., 2009b; Xiao et al., 2015). Moreover, PFASs via food chain transfer from soil to plant, and then enter into humans or animals (Navarro et al., 2017; Yang et al., 2014). Therefore, study of PFASs in soil is significant to understand the fate and transport of PFASs in the environment and conduct risk assessment. Life cycle analysis is an effective tool, which can trace transport pathways of pollutants from manufacture to the environment. Analysis of environmental fate of some metals and persistent organic pollutants (POPs) has been conducted, such as polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs) and PFOA (Zhang et al., 2011; Lee et al., 2015; Ventura et al., 2015; Kodavanti and Loganathan, 2017; Meng et al., 2017). Based on life cycle analysis of PFASs in China, it was meaningful to use this method at regional level.

The Bohai Sea is the innermost gulf of the Yellow Sea on the coast of Northern China. Due to unique resources and geographical advantages, coastal area of the Bohai and Yellow Seas are a significant economic zone, no matter for China or South Korea and Japan. With rapid urban expansion in the coastal area, environmental quality has declined, pollution range has expanded and ecological damage has increased (Khim et al., 2017; Liu et al., 2012; Strokal et al., 2014). Therefore, traditional environmental problems such as eutrophication and metal pollution became more severe, while new environmental problems caused by emerging pollutants such as PFASs appeared. A wide range of industries are distributed in this urbanizing area, including textiles, metal plating, production of fire-fighting chemicals and semiconductor industries, some of which are associated with industrial sources of PFOA, PFOS and related substances in China (Xie et al., 2013b; Zhang et al., 2012). Moreover, this study area is one of the most populated and urbanized regions in China, where the emission of PFOS, PFOA and related substances from domestic sources is expected to be considerable (Li et al., 2015; Xie et al., 2013a).

Soil serves as one of the important sources and sinks of PFASs. It was reported that PFOS in soil contributed 53.0% of the total inventory in the Bohai coastal area based on a model estimation (Liu et al., 2015). To date, research on PFASs mainly focused on soil impacted by either application of contaminated sludge or nearby fluorochemical facilities. Therefore, identification of sources was needed in this area due to the large influence from soil.

The objectives of this study were to 1) systematically investigate pollution of PFASs in soil from coastal area of the Bohai and Yellow Seas, 2) identify point and diffuse sources of PFASs for every city along the coastal area, 3) establish the relationship between source and actual detection in soil, 4) evaluate the influence of industrialization using specific industry data.

2. Materials and methods

2.1. Sampling collection

The sampling campaign was conducted from 21 cities in Liaoning, Hebei, Tianjin, Shandong and Jiangsu along the Bohai and Yellow Seas in September 2013. Considering different land use and surroundings, sampling points were generally uniformly distributed. The sampling interval was approximately 50 km. Each sample consisted of five sub-samples within an area of 50 m × 50 m. Samples were collected using a stainless steel trowel that had been rinsed with methanol and stored in clean polypropylene (PP) bags. Finally, 153 surface (10 cm) soil samples were collected covering a

total area of 213,000 km² (Fig. S1). All samples were dried in air, homogenized with a porcelain mortar and pestle, sieved with a 2 mm mesh, and stored in PP bags at room temperature until extraction.

2.2. Chemicals and reagents

The external standards of 12 PFASs, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUDA), perfluorododecanoic acid (PFDoA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS, and the international standards regarding PFOA [1, 2, 3, 4 ¹³C] and PFOS [¹⁸O₂], had purities of >98% (Wellington Laboratories, Canada). HPLC grade methanol and acetonitrile (ACN) were purchased from J.T. Baker (Phillipsburg, NJ, USA). Ammonium acetate (~98%), anhydrous sodium sulfate, hydrochloric acid (HCl, ≥37%), sodium hydroxide (NaOH), and ammonia (28%–30% NH₃ basis) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Milli-Q water was obtained from a Milli-Q gradient A10 (Millipore, Bedford, MA, USA).

2.3. Extraction and cleanup

Extraction of PFASs was accomplished using a method similar to previously described method (Wang et al., 2016a). Briefly, 2.0 g of sample was transferred to a 50 mL PP tube, spiked with 5 ng internal standard and 2 mL of 100 mM NaOH/ACN with ultrasonic agitation. Then 20 mL ACN was added with vibrating 30 min at 250 rpm. 0.1 mL of 2M HCl was added and the target was separated by centrifugation at 3000 rpm for 15 min. The supernatant was transferred to a new 50 mL PP tube. This process was repeated once with 10 mL ACN. A total of 30 mL ACN supernatant was evaporated to 1 mL under a gentle flow of high-purity nitrogen. The 1 mL extracts were further purified by using ENVI-Carb and SPE cartridges.

The ENVI-Carb cartridge was purified with 1 mL menthol 3 times. 1 mL ACN extracts flowed through the cartridge and collected. Then 1 mL menthol was used to wash the PP tube and cartridge three times, respectively. Totally, 7 mL elution was collected and transferred to 100 mL PP tube, diluted to 100 mL with Milli-Q water and extracted with the OASIS WAX-SPE cartridge. The SPE cartridge was preconditioned with 4 mL of 0.1% NH₄OH in methanol, 4 mL methanol and 4 mL Milli-Q water. Then 100 mL sample was loaded into the cartridge. The cartridge was washed with 20 mL Milli-Q water, 4 mL of 25 mM ammonium acetate (pH = 4), allowed to run dry, and eluted with 4 mL methanol and 4 mL of 0.1% ammonia in methanol. The eluents were concentrated to 0.5 mL under high purity nitrogen and passed through a nylon filter (0.2 μm), then transferred into a 1.5 mL auto-sampler vial fitted with PP cap for HPLC analysis.

2.4. Instrumental analysis

All PFASs were separated and quantified via Agilent 1290 Infinity HPLC System coupled to an Agilent 6460 Triple Quadrupole LC/MS System (HPLC-MS/MS) operated in the negative electrospray ionization (ESI-) mode. The HPLC-MS/MS was fitted with a Agilent ZORBAX Eclipse Plus C18 (2.1 × 100 mm, 3.5 μm particle size) analytical column, and a suitable guard column (Agilent 1290 Infinity In-line filter with 0.3 μm SS frit) was used to prevent instrument background contamination. 2 mM ammonium acetate (A) and acetonitrile (B) were used as mobile phases.

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