



Are levels of perfluoroalkyl substances in soil related to urbanization in rapidly developing coastal areas in North China?



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ABSTRACT

Concentrations of 13 perfluoroalkyl substances (PFASs) were quantified in 79 surface soil samples from 17 coastal cities in three provinces and one municipality along the Bohai and Yellow Seas. The Σ PFASs concentrations ranged from less than limitation of quantification (LOQ) to 13.97 ng/g dry weight (dw), with a mean of 0.98 ng/g dw. The highest concentration was observed along the Xiaoqing River from Shandong province, followed by that from the Haihe River in Tianjin (10.62 ng/g dw). Among four regions, Σ PFASs concentrations decreased in the order of Tianjin, Shandong, Liaoning and Hebei, which was consistent with levels of urbanization. Fluorine chemical industries allocated in Shandong and Liaoning played important roles in terms of point emission and contamination of PFASs, dominated by perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). Intensive anthropogenic activities involved in urbanization possibly resulted in increasing releases of PFASs from industrial and domestic sources.

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1. Introduction

Due to many desirable properties such as surface activity, thermal stability, acid resistance, and amphiphilicity (Kissa, 2001), perfluoroalkyl substances (PFASs) have been widely used as surfactants and surface protectors in carpets, furniture, paper, food containers, fabrics, and upholstery. They have also been applied as performance chemicals in products such as fire-fighting foams, floor polishes, and shampoos (Giesy and Kannan, 2001). They are now considered emerging pollutants, whose environmental persistency, bioaccumulation, global distribution and toxicity (Conder et al., 2008; Giesy et al., 2010; Schuetze et al., 2010; Zushi et al., 2010) have raised increasing concerns. PFASs were reported to be widespread in the environment (Giesy and Kannan, 2001, 2002) and subsequently detected in aquatic systems (Fujii et al., 2007; Rayne and Forest, 2009) and wildlife (Kannan et al., 2002; Houde et al., 2006; Fatihah et al., 2009). PFASs in soils can be transported to the atmosphere, surface water and groundwater

through volatilization, diffusion, leaching and mass flow (Armitage et al., 2009). Moreover, PFASs can biomagnify and accumulate through the food chain to wildlife and humans. The adverse effects of PFASs on ecosystem and human health as well as secondary release of PFASs from soil are still of long-term public concerns. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), two predominant PFASs frequently detected in the environment, have received great attention in recent years. PFOS and its salts have recently been listed as “persistent organic pollutants” (POPs) under the Stockholm Convention. However, exemptions were made to allow their continued production and use in China (Wang et al., 2009b). China began large-scale production of PFOS and related chemicals in 2003. Before 2004, the total production of PFOS and related chemicals in China was less than 50 tons, whereas in 2006, fifteen Chinese enterprises produced a total of more than 200 tons with 100 tons exported (Bao et al., 2009).

The coastal and estuarine areas of the Bohai and Yellow Seas, investigated in the present study, include seventeen coastal cities in Tianjin, Hebei, Shandong, and Liaoning. The urbanization and industrialization in the coastal regions are progressing dramatically along with rapid economic development. These intensive anthropogenic activities have severely deteriorated environmental

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quality, especially along the coast (Qiu et al., 2009; Tan et al., 2009). Emerging pollutants such as PFASs have become urgent environmental issues due to their extensive sources, high level of hazard, and difficulty of monitoring and controlling. Results of previous studies indicated that emissions of PFOS were greater in more urbanized eastern coastal regions of China (Xie et al., 2013a,b). Intensive industries including textile, printing and electroplating have led to releases of PFASs, especially those based on PFOS (Huang et al., 2010). The fluorine industry parks located in Liaoning and Shandong provinces have released PFASs (Wang et al., 2013, 2014). Since 2008, we have been conducting systematic research of organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and heavy metals in environmental matrices along the Bohai Sea. It was found that industrialization and urbanization were strongly related to their pollution and distribution (Hu et al., 2010; Chen et al., 2011; Wang et al., 2011a). The Yellow River, Haihe River and Liaohe River systems are the most important water sources in this region, and most of the river systems eventually flow into the Bohai and Yellow Seas. Rapid economic development has generated, and continues to generate increasing amounts of municipal, industrial and agricultural wastes, which eventually accumulate in the Bohai and Yellow Seas. Bohai Sea is currently one of the most polluted seas in China (Zhang et al., 2006; Tan et al., 2009; Luo et al., 2010).

Our previous studies focused mainly on classic persistent toxic substances (PTS) such as heavy metals, PAHs, and OCPs in soils and sediments. PFASs in water were also reported (Hu et al., 2010; Luo et al., 2010; Chen et al., 2011; Wang et al., 2011b; Jiao et al., 2012). In this study, the concentrations and distribution of emerging pollutants PFASs were determined in soils from coastal and estuarine areas of the Bohai and Yellow Seas. The relationship between the PFASs concentrations in soil and the levels of urbanization was also analyzed. Using a systematic approach, this study may help identify potential sources of pollutants and provide information for future management and soil remediation. There are currently very few studies of PFASs in soil. For the first time, we investigated spatial distribution and potential sources of PFASs in soil samples taken from this rapidly developing coastal region.

2. Materials and methods

2.1. Sampling design and collection

The study area included three provinces and one municipality along the Bohai and Yellow Seas, i.e. Liaoning, Hebei, Tianjin and Shandong. A total of seventy-nine surface soils were collected from estuarine and coastal areas adjacent to the Bohai and Yellow Seas, including twenty-two from Liaoning, nine from Hebei, eight from Tianjin and forty from Shandong (Fig. S1). Surface (top 0–20 cm) soil samples were collected using a stainless steel trowel that had been rinsed with methanol. Each sample was a composite of five sub-samples (each weighed about 500 g) collected from the center and four corners of an area of 100 × 100 m². Sampling information including location, land use and detailed description were summarized in Table S1. Samples were then transferred and stored in clean polypropylene (PP) bags. Duplicates and field blanks were collected in each city and analyzed with laboratory and procedural blanks. All samples were dried in air, homogenized with a porcelain mortar and pestle, sieved with a 2 mm mesh, and stored in 250 mL PP bottles at room temperature until extraction.

2.2. Chemicals and reagents

The detailed descriptions on chemicals and reagents were available in [Supplementary Material](#).

2.3. Extraction and cleanup

PFASs were extracted using methods similar to those described previously (Wang et al., 2013). Briefly, 2.5 g of sample was transferred to a 50 mL PP tube, and moistened by 2 mL Milli-Q water with vortexing. Then 1 mL of 0.5 M TBAHS, 2 mL of 25 mM sodium acetate and 1 ng mass-labeled internal standards (PFOA [1, 2, 3, 4 ¹³C] and PFOS [¹⁸O₂]) were added into the PP tube. The mixture was shaken at 700 r/min for 5 min. Subsequently, 5 mL of MTBE was added and shaken for 20 min. After centrifuging for 20 min at 3500 r/min, the supernatant MTBE was collected. This process was repeated twice which produced a final volume of 15 mL MTBE wash. The supernatant was evaporated to dryness under a gentle flow of high-purity nitrogen, and reconstituted in 1 mL methanol. The 1 mL elution was transferred to 50 mL PP tube, brought to 50 mL with Milli-Q water and extracted with the SPE cartridge.

The SPE cartridge was preconditioned with 4 mL of 0.1% ammonia in methanol, 4 mL methanol and 4 mL Milli-Q water. 50 mL sample was loaded into the cartridge. The cartridge was washed with 20 mL Milli-Q water, 4 mL of 25 mM sodium acetate, allowed to run dry, and eluted with 4 mL methanol and 4 mL of 0.1% ammonia in methanol. The eluents were collected, combined, and concentrated to 1 mL under a gentle stream of high purity nitrogen and then filtered through a 0.2 μm nylon filter into a 1.5 mL autosampler vial fitted with PP cap for HPLC analysis.

2.4. Instrumental analysis and quantitation

All PFASs were analyzed using an Agilent HP 1200 high performance liquid chromatography system (HPLC) equipped with an Applied Bioscience SCIEX 3000 tandem mass spectrometer (HPLC-MS/MS). Quantification was performed using Analyst 1.4.1 software provided by SCIEX. The detailed descriptions on instrumental

Table 1

QA/QC information of 13 PFASs including monitoring transitions (MT), limit of detection (LOD), limit of quantification (LOQ), matrix spike recovery (MSR) and detection ratio.

Analyte	MT	LOD ng/g	LOQ ng/g	MSR %	Detected ratio ^a (%)
Perfluorobutanoic acid (C4, PFBA)	213 → 169	0.05	0.05	100 ± 5	14 (18)
Perfluoropentanoic acid (C5, PFPeA)	263 → 219	0.01	0.03	104 ± 3	10 (13)
Perfluorohexanoic acid (C6, PFHxA)	313 → 269	0.01	0.01	110 ± 3	21 (27)
Perfluoroheptanoic acid (C7, PFHpA)	363 → 319	0.01	0.02	96 ± 6	20 (25)
Perfluorooctanoic acid (C8, PFOA)	413 → 369	0.05	0.05	100 ± 11	57 (72)
Perfluorononanoic acid (C9, PFNA)	463 → 419	0.05	0.05	109 ± 2	39 (49)
Perfluorodecanoic acid (C10, PFDA)	513 → 469	0.01	0.01	103 ± 7	33 (42)
Perfluoroundecanoic acid (C11, PFUdA)	563 → 519	0.01	0.02	90 ± 4	41 (52)
Perfluorododecanoic acid (C12, PFDoA)	613 → 569	0.01	0.01	89 ± 4	17 (22)
Perfluorobutane sulfonate (C4, PFBS)	299 → 99	0.05	0.05	119 ± 4	17 (22)
Perfluorohexane sulfonate (C6, PFHxS)	399 → 99	0.01	0.01	114 ± 8	0 (0)
Perfluorooctane sulfonate (C8, PFOS)	499 → 99	0.05	0.05	117 ± 2	49(62)
Perfluorodecane sulfonate (C10, PFDS)	599 → 99	0.01	0.02	86 ± 6	0 (0)

^a Number of samples detected and % – occurrence in parenthesis given.

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