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.

analysis were available in [Supplementary Material](#).

2.5. Quality control and quality assurance

For quality control and quality assurance, the use of Teflon coated lab-ware was avoided during all steps of sample preparation and analysis to minimize contamination of the samples. Field blanks, laboratory blanks (including procedural blanks and solvent blanks) and matrices spiked with the standard solution (2.0 ng/g dw) were analyzed. Procedural blanks using anhydrous sodium sulfate in place of soil were analyzed with every set of samples and solvent blanks using 100% methanol were run every 4–5 samples to check for carryover and background contamination. Concentrations of all target PFASs in all field and laboratory blanks were less than the limit of detection (LOD), which was defined as 3 times of signal-to-noise ratio (S/N). And the limit of quantification (LOQ) was set as 5 times of S/N. Recoveries of PFASs were determined in the range from $86 \pm 6\%$ to $119 \pm 4\%$. Detailed QA/QC measurements of PFASs in soil are given in [Table 1](#).

2.6. Statistical analysis

All statistical analyses were performed with SPSS Statistics V20.0 (SPSS Inc, USA). A statistical distribution test called P–P plots was carried out to test the normal distribution of raw data in order to ensure the data sufficient for further analysis ([Fig. S2](#)). Spatial distributions of PFASs were analyzed using ArcGIS V10.0 (ESRI).

3. Results and discussion

3.1. Occurrence of soil PFASs and association with urbanization

Levels of Σ PFASs in soils from coastal and estuarine areas with different urbanization levels along the Bohai and Yellow Seas are summarized in [Table 2](#). Urban population ratio, GDP per capita and tertiary industry ratio were collected to reflect the level of urbanization of each city. Higher values of the three indices tended to represent higher levels of urbanization ([Chen et al., 2013](#)).

Commercial products were one of the important domestic sources of PFASs in cities ([Xie et al., 2013a](#)), and the urban population ratio and GDP per capita could be a surrogate for the extent of usage of these products. In general, urbanization of Tianjin was apparently higher than that of the other three regions. Mean concentrations of Σ PFASs in the four regions were as follows: Tianjin (3.55 ng/g dw) > Shandong (0.93 ng/g dw) > Liaoning (0.52 ng/g dw) > Hebei (0.09 ng/g dw). Soil samples from Tianjin were collected from Binhai district, which is one of the important industrial regions with the most rapid development and relatively greater level of urbanization. Concentrations of other pollutants, such as heavy metals, OCPs, and PAHs were relatively higher in this region as well ([Luo et al., 2010](#); [Wang et al., 2009a](#); [Jiao et al., 2012](#)).

Among the seven cities in Shandong province, the highest concentration of Σ PFASs was observed in Dongying, with a mean of 2.60 ng/g dw. The GDP per capita of Dongying (\$21,162) was higher than that of other cities as well. The secondary industry contributed greatly to the higher GDP of Dongying, while its tertiary industry ratio (24.7%) was smaller as compared to other cities in Shandong. The local dominant industries, including textile and papermaking, might be the largest industrial sources of PFASs ([Davis et al., 2007](#); [Xie et al., 2013b](#)). The highest concentration of Σ PFASs (13.97 ng/g dw) in all 79 soil samples was also observed in Dongying, which further proved the impacts of textile and papermaking industries. Concentration of Σ PFASs in soils from Binzhou (0.91 ng/g dw) ranked the second. One of the largest Chinese chemical plants is situated in Binzhou, which discharges massive pollutants to the environment. Concentrations of Σ PFASs from Dongying and Binzhou were only lower than those from the Binhai district of Tianjin, but higher than those from other cities. As the second largest city in Shandong province, Qingdao is highly urbanized. The urban population ratio and tertiary industry ratio are as high as 63.1% and 47.8%, respectively. Concentrations of Σ PFASs in soils of Qingdao were relatively high, with a mean of 0.73 ng/g dw. Compared with Dongying and Binzhou, secondary industries contributed a smaller proportion to pollution in Qingdao. However, intensive human activities possibly resulted in releases of PFASs from domestic sources such as packing materials, domestic

Table 2
Soil Σ PFASs (ng/g dw) and urbanization levels in coastal and estuarine areas of the Bohai and Yellow Seas.

Province	City	Type of area			Σ PFASs			Indicator of urbanization		
		Urban	Suburban	Rural	PFOA	PFOS	Total	Urban population ratio (%)	GDP per capita (USD)	Tertiary industry ratio (%)
Liaoning	Dandong	0.43(1) ^a	— ^b	0.26(3)	nd ^c	nd	0.30	43.0	5412	35.1
	Dalian	—	—	0.12(4)	nd	nd	0.12	62.5	15368	41.5
	Yingkou	1.26(1)	—	1.02(2)	0.08	0.26	1.10	48.2	7382	37.0
	Panjin	0.23(1)	—	0.23(1)	0.05	nd	0.23	66.8	12074	22.8
	Jinzhou	0.71(1)	0.41(1)	0.68(3)	0.21	0.01	0.63	40.5	5265	35.1
	Huludao	0.33(1)	0.21(1)	1.20(2)	0.20	0.11	0.74	31.6	3632	37.2
	Total	0.59(5)	0.31(2)	0.53(15)	0.10	0.06	0.52			
Hebei	Qinhuangdao	0.27(1)	0.39(1)	0.23(1)	0.09	nd	0.30	41.6	5221	47.3
	Tangshan	—	0.03(2)	0.05(4)	nd	nd	0.04	33.5	10529	31.0
	Total	0.27(1)	0.15(3)	0.09(5)	0.03	nd	0.09			
Tianjin	Binhai	6.15(2)	6.98(1)	1.82(5)	0.41	1.88	3.55	71.7	40206	31.0
	Total	6.15(2)	6.98(1)	1.82(5)	0.41	1.88	3.55			
Shandong	Dezhou	0.59(1)	—	0.56(2)	0.25	0.15	0.55	30.7	4985	33.9
	Binzhou	—	0.94(2)	0.95(4)	0.58	0.11	0.91	37.7	7103	36.7
	Dongying	0.40(2)	—	3.50(5)	2.32	0.10	2.60	43.3	21162	24.7
	Weifang	0.22(1)	0.85(1)	0.65(4)	0.33	0.12	0.59	52.4	5706	34.5
	Yantai	0.44(3)	0.33(1)	0.48(9)	0.14	0.13	0.42	50.1	10338	34.9
	Weihai	—	—	0.33(2)	0.06	0.11	0.31	51.4	12235	37.9
	Qingdao	—	0.34(1)	0.97(2)	0.26	0.17	0.73	63.1	12691	47.8
	Total	0.41(7)	0.74(5)	1.11(28)	0.63	0.12	0.93			

^a Sample number in corresponding urbanization gradient.

^b No sample in corresponding urbanization gradient.

^c Not detectable, means concentration less than LOQ.

wastewater and daily commodities.

In Liaoning province, soils were collected from six cities near the Bohai Sea. Intensity of urbanization in Dalian was the greatest with an urban population ratio of 62.5% and a tertiary industry ratio of 41.5%. Dalian is the pioneer city to adopt environmentally friendly urban planning and strict environmental management. By adjusting industrial structures, heavy-polluting sections are constantly eliminated and the proportion of chemical industry is decreasing. These activities resulted in lower concentrations of Σ PFASs in Dalian when compared with those of other coastal cities in Liaoning. In Liaoning province, the highest concentration of Σ PFASs (1.10 ng/g dw) was observed in Yingkou, one main area of the Liaohe River Basin. As a major water-receiving body, the Liaohe River system is influenced by sewage from the surrounding cities, and receives about 2 billion tons of industrial and domestic wastewater annually (Huang et al., 2012).

In Hebei, soils from Qinhuangdao and Tangshan, had relatively lower concentrations of Σ PFASs, with mean values of 0.21 and 0.04 ng/g dw, respectively. Although Tangshan is an important industrial city, dominated by the iron and steel industry, its industries do not cause as much PFAS pollution as the chemical industry. Generally, higher level of urbanization usually represents a decreasing industry ratio via the adjustment of industrial structure, and the pollution of PFASs usually reduces accordingly. Meanwhile, urban population increases with urbanization leading to domestic emissions of PFASs. However, the domestic sources of emission account for only a small proportion (<10%) of the gross sources (Xie et al., 2013a,b).

3.2. PFASs in soils along the urbanization gradients

Spatial patterns of relative concentrations of Σ PFASs varied among urban, suburban and rural areas, and among the four regions (Fig. 1). Proportions of Σ PFASs in soils from the urban (39.0%) and rural (36.4%) areas in Liaoning province were relatively higher than those in suburban soils (24.6%). Liaoning is an important base of the northeast traditional industries, currently at the transitional stage of industrial development. Jinzhou and Huludao have been two cities with the most intensive chemical industry in China since the 1960s. There are still oil refining plants, chemical plants, and smelting plants in these regions (Wang et al., 2011b). PFASs have

been reported with higher concentrations in urban areas than in rural areas, which indicates that apart from industrial activities, releases from consumer products in urban areas are potential sources of PFASs as well (Kim and Kannan, 2007; Ju et al., 2008).

Proportion of Σ PFASs in soils from Hebei province was greater in urban (60.0%), than suburban (26.7%) or rural areas (13.3%), with mean concentrations of 0.27 ng/g dw, 0.12 ng/g dw and 0.06 ng/g dw, respectively. Hebei province has been relatively less urbanized than the other three provinces. Most industries are still situated in urban areas, and agricultural nonpoint source is still the main source in rural areas. Local industries are unlikely to cause serious pollution of PFASs, while domestic emission is also a main source comparing with other industrial regions.

Concentration of Σ PFASs was the highest (6.97 ng/g dw) in soils of suburban area of Tianjin and a relatively higher mean concentration of 6.15 ng/g dw was observed in soils of urban area. The suburban area provides service facilities, e.g. wastewater treatment plants, for the urban area, and many emerging industrial zones, especially for the high tech industries. The Tianjin Binhai district is one of the most important industrial areas in Northern China. Intensive economic development and urbanization in this area have severely deteriorated environmental quality (Guo et al., 2011; Wang et al., 2011b). However, Shandong province exhibited completely different distribution of PFASs. Rural soils had the highest concentration of Σ PFASs (1.11 ng/g dw, 49.1%), while the proportions in urban and suburban soils were only 18.1% and 32.7%. Shandong is one of the fastest developing provinces. After intensive development of urban areas, more industries are moving from urban to rural and/or suburban areas in order to obtain adequate and cheaper land and labors. This has led to the industrial emissions of PFASs, which gradually become the main source of pollution in rural and suburban areas (Kim et al., 2012).

3.3. PFASs in soils along the coastal and estuarine rivers

For areas along the coastal and estuarine rivers adjacent to the north Bohai Sea, the highest concentration of Σ PFASs (1.81 ng/g dw) was observed in soil from Huludao (Fig. 2). The four detected PFASs, including perfluorononanoic acid (PFNA), PFOA, perfluoroundecanoic acid (PFUdA) and PFOS, had relatively similar concentrations. The second highest concentration of Σ PFASs was 1.26 ng/g dw, which was dominated by PFNA (0.96 ng/g dw). This site is located in the city of Yingkou and sample was collected from the estuary of the Liaohe River, which flows through the Bayuquan district of Yingkou. The Bayuquan district is one of the most rapidly developing regions in the Liaodong Bay with several large industrial parks. The industries in these parks include textile, chemistry, machinery, home appliances, etc. Some PFASs may be released in the production activities.

Soil samples along the five rivers adjacent to the Tianjin coast were severely polluted. Concentrations of Σ PFASs along these river systems were as follows: Haihe River (6.16 ng/g dw) > Yongding River (3.83 ng/g dw) > Ziya River (2.07 ng/g dw) > Chaobai River (1.31 ng/g dw) > Duliujian River (1.27 ng/g dw). Haihe River was found to be one of the most polluted rivers in terms of PFASs or other pollutants (Luo et al., 2010; Wang et al., 2009a; Jiao et al., 2012; Li et al., 2011). The intense pollution was derived from rapid development of the Beijing-Tianjin metropolitan region, especially the Tianjin Binhai district. The highest concentration of Σ PFASs (10.63 ng/g dw) was observed in the estuary of the Haihe River and the Bohai Bay, with a large contribution of 88.15% by PFOS. The Binhai district has been subjected to anthropogenic influences as a result of rapid urbanization and industrialization. The relatively great concentrations of Σ PFASs indicated an input from industrial effluent as well as atmospheric deposition. Furthermore,

Fig. 1. Concentrations of Σ PFASs (ng/g dw) in soils along different urbanization gradients.

Fig. 2. Spatial distributions of sample locations and related concentrations of Σ PFASs (ng/g dw) along coastal and estuarine areas of the Bohai and Yellow Seas.

the Haihe Watershed contains a variety of industries including chemical and biochemical products manufacturing, and receives industrial and domestic discharges mainly from Tianjin and Beijing.

For samples of soils along the coastal and estuarine rivers adjacent to the south Bohai Sea and Yellow Sea, mainly from Shandong province, the concentrations of Σ PFASs along the Xiaoqing River (5.53 ng/g dw), Tuhai River (1.25 ng/g dw), Shahe River (0.98 ng/g dw) and Jialai River (0.98 ng/g dw) were higher than those along the other 14 rivers. The Xiaoqing, Shahe and Jialai Rivers flow into the Laizhou Bay and contribute greatly to pollution. The most severely polluted area occurred in the downstream of the Xiaoqing River, with a concentration of 13.97 ng/g dw. PFOA was the dominant pollutant and accounted for more than 98.7% of Σ PFASs. PFOA is used as the surfactant in the treatment of paper and textile and directly causes serious pollution locally. Simultaneous investigation indicated that facilities along the Xiaoqing River and its tributaries exhibited the greatest emissions of wastes (Wang et al., 2014; Zhu et al., 2014). However, samples of soil and other media such as water and sediments could not be collected directly from the manufacturing facilities to verify the presumed source of PFOA. Therefore, more research is needed to determine its exact origin.

3.4. Patterns of relative concentrations of Σ PFASs in soils

The compositions of Σ PFASs in soils along the coast and estuary of the Bohai and Yellow Seas are summarized in Fig. 3. The compositions of the four regions were completely different. Generally, PFOA and PFOS were the dominant PFASs. Other detected PFASs were mainly longer-chain perfluorocarboxylic acids (PFCAs), including PFNA, PFUDA and perfluorododecanoic acid (PFDDoA).

Longer-chain PFCAs are more easily adsorbed to solids (Higgins et al., 2005; Li et al., 2010). In Liaoning province, PFNA and PFUDA contributed 39.1% and 30.8% of Σ PFASs, respectively, while PFOS and PFOA only accounted for 12.9% and 17.2%, respectively. While in Hebei province, only longer-chain PFCAs such as PFOA, PFNA and PFUDA, were detected. In this region, releases of PFASs were mainly from domestic products. In the Tianjin municipal region, PFOS accounted for 53.1% of Σ PFASs. In general, PFOS is derived from industrial emission, indicating that factories in Tianjin discharged relatively large amounts of PFOS. In addition, PFOA, PFUDA and PFDDoA accounted for approximately half of the concentration of Σ PFASs. In Shandong province, PFOA (66.3%) and PFOS (13.2%) were the major components of Σ PFASs, especially PFOA. The greater detection ratio of PFOA was mainly contributed by pollutants from the Xiaoqing River. Meanwhile, other PFASs were detected in Tianjin and Shandong, which were released from different types of industries, especially chemical industry. The difference among the four regions revealed that the pollution was mainly caused by industrial sources, because there was not much difference in domestic sources under current urbanization.

In terms of urbanization gradients, the detected PFASs were mostly consistent in the same region, but the proportions were distinct among the three gradients of urbanization. Major industries caused the differences among the four regions. The locations of these factories led to the differences among urban, suburban and rural areas. In Tianjin and Shandong, concentrations of PFOS decreased from urban, to suburban to rural areas, but concentrations of PFOA increased along the same gradient. The trend of PFOS indicated that chemical industry was the primary source. However, the increased trend of PFOA in Shandong was mainly caused by the increasing number of papermaking and

Fig. 3. Compositions of individual PFASs in soils according to urbanization and river.

textile factories.

The most important source of contaminants in soils along rivers is irrigation with river water. Polluted rivers are likely to increase the contamination of soils. Thus, investigation of PFASs in soils could be useful for a long-term, integrative measure of the status of PFASs in rivers (Naile et al., 2010; Wang et al., 2011b; Meng et al., 2013). Concentrations of PFASs in rivers are mainly derived from upstream regions of rivers and surrounding domestic and industrial sources. Transport of PFASs along rivers in Shandong was the most obvious, which can be exemplified by the variation of PFOA and PFOS. This indicated the contribution of PFASs from upstream. Contributions of PFASs from upstream areas in Liaoning, Hebei and

Tianjin were relatively smaller than the surrounding sources.

3.5. PFASs in soils under different land uses

Soil samples were classified into six groups according to land use, including grain ($n = 27$), grass ($n = 13$), barren ($n = 18$), woods ($n = 11$), cotton ($n = 7$) and fruit ($n = 3$) (Table S5). Concentrations of $\sum$ PFASs in soils under different land uses showed obvious difference (Fig. 4). In Tianjin, $\sum$ PFASs (6.16 ng/g dw) in barren land were the highest, followed by $\sum$ PFASs in grassland (3.09 ng/g dw). These barren lands were located in surroundings of factories, so the industrial emissions may be the main contributor. $\sum$ PFASs in grassland were detected with much higher levels in Liaoning (0.71 ng/g dw) and Shandong (2.11 ng/g dw). $\sum$ PFASs in grain land (nd–2.07 ng/g dw) and wood land (nd–2.51 ng/g dw) showed similar levels in the four regions. The relatively low $\sum$ PFASs levels in most grain lands (with the exception of those from the Haihe River and the Xiaoqing River) indicated no serious pollution to food source. Therefore, it is necessary to change the type of land use or prohibit river irrigation at these sites with relatively high levels of $\sum$ PFASs. Cotton soils and fruit soils were only collected in Shandong. $\sum$ PFASs from the two different lands were 0.93 and 0.42 ng/g dw, respectively.

4. Conclusion

The urbanization and industrialization in the coastal region are growing dramatically along with the rapid economic development in China. As a result, emerging pollutants such as PFASs produced in the processes of production and consumption, have become new and urgent environmental issues. Plenty of old industrial areas coexist with rapidly urbanized areas along the coastal region of the

Fig. 4. Concentrations of $\sum$ PFASs (ng/g dw) in soils under different land uses.

Bohai and Yellow Seas, which result in increasing pollution of PFASs. PFASs in soils from Tianjin and Shandong with higher levels of urbanization showed relatively higher concentrations. With the development of urbanization, factories are constantly moving from urban areas to rural areas, which can raise emission of PFASs in rural areas as well. Rural areas, being important bases for crop production, deserve more attention. In general, PFOA and PFOS were the dominant PFASs in the studied area, especially in Tianjin and Shandong. PFOS was mainly emitted from chemical plants, and PFOA mainly came from paper-making and textile industries. This study would provide valuable information for management and control of the emerging pollutants in the rapidly developing coastal region. Further detailed work with more intensive sampling effort over time is recommended to identify any shifts in production to shorter chained or lesser fluorinated PFASs. Such approach would help identify trends and sources, and evaluate control measures to reduce soil and riverine discharge of PFASs into the coastal and marine ecosystem.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2015.01.022>.

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