



Occurrence, spatial and temporal distributions of perfluoroalkyl substances in wastewater, seawater and sediment from Bohai Sea, China[☆]



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ABSTRACT

In this study, surface seawater and sediment samples were collected from Bohai Sea, China, to investigate the temporal and spatial distributions of perfluoroalkyl substances (PFASs) in that area. The total concentrations of PFASs in seawater and sediment samples ranged from below method limit of quantification (<MLQ) to 99.4 ng/L, and from 0.33 to 2.78 ng/g dw, respectively. PFOA was the predominant PFASs in both of surface seawater and sediment samples, with a median concentration of 4.97 ng/L in seawater and 0.24 ng/g dw in sediment sampled in July, respectively. Seasonal variation of the total PFAS concentrations was found in seawater samples, but not in the sediments. The concentrations of the total measured PFASs in water samples from drain outlets ranged from 103 ng/L to 443 ng/L, which was four times higher than that in seawater from the Bohai Sea, suggesting that discharge of wastewater from drain outlets was responsible for the contamination of PFASs in Bohai Sea area.

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs), such as perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFASs), are a class of synthetic compounds where all or part of the C–H bonds have been replaced by C–F bonds. PFASs have excellent thermal and chemical stability, as well as surface-active properties. Therefore, they are widely used in the past six decades as additives in surface coatings of carpet, leather, papers, textiles, fire-fighting foams, pesticides, etc. (Lindstrom et al., 2011). Their properties also make them highly persistent in the environment and

accumulative in human and wildlife (Kelly et al., 2009; Li et al., 2013). Due to their high persistency, they are ubiquitous in various environmental matrices worldwide, such as water, soil, sediment, sludge and even the polar ice caps (Chen et al., 2012b; Lau, 2012; Loi et al., 2013; Post et al., 2012). Meanwhile, this class of compounds has been shown to have hepatic, developmental, immune and endocrine toxicity in experimental animals (Wang et al., 2010). In 2009, perfluorooctane sulfonic acid (PFOS) and its salts, one representative of PFASs, were listed in the Stockholm Convention as Persistent Organic Pollutants.

Marine environment was considered as a sink of PFASs. Their levels and spatial distribution in the marine environment worldwide have been investigated. Ahrens et al. (2010a) investigated distribution of PFASs in seawater from Northern Europe, Atlantic Ocean, and Southern Ocean, and found that industrial areas act as source of PFASs, while ocean water is an important sink as well as the transport medium. Naile et al. (2010) found the relatively great concentrations of PFASs in water and sediment from estuarine and coastal areas of Korea, suggesting that further studies characterizing PFASs and their potential risk are needed. Production and usage of PFASs in China have increased rapidly in recent years due

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to a shift of the production bases of the PFAS-related industries from developed countries to developing countries. A large part of the total PFAS outputs in China are from coastal provinces and cities, such as Liaoning which is adjacent to the Chinese Bohai Sea. The Bohai Sea Economic Rim is a highly urbanized and industrialized region in North China. Hundreds of drain outlets discharge and more than forty rivers flow into this sea area. However, the Bohai Sea is semi-enclosed, with limited seawater exchange. Therefore, the researchers have studied PFAS pollution in that area. Chen et al. (2011) found that sediment was an important sink for perfluoroundecanoic acid (PFUnDA) through the investigation of PFASs in water and sediment from coastal northern Bohai Sea. Gao et al. (2014) had also investigated the PFASs in marine sediments from the Bohai Sea. However, few studies have been conducted in the levels of short-chain (carbon length < 7) and long-chain (carbon length > 12) PFASs in this area. Moreover, information on seasonal variation of PFAS levels in seawater and PFAS pollution status in drain outlets is still absent and worthwhile to be further studied.

The specific objectives of this study are to evaluate the spatial distribution of PFAS pollution and their seasonal variation in the Bohai Sea, especially the short-chain and long-chain PFASs, and to investigate PFAS levels in water from drain outlets which flow directly into the Bohai Sea. To accomplish these goals, a total of 19 PFASs, including 13 PFCAs and 4 PFASAs, as well as two precursor chemicals in surface seawater, marine sediment and drain outlet samples from Chinese Bohai Sea were analyzed.

2. Materials and methods

2.1. Study area and sample collection

A sampling map and sampling sites are shown in Fig. 1. Surface

water and sediment samples were collected from the Bohai Sea, China, covering a total area of about 77,000 km². There are three bays in this sea area, named Liaodong Bay, Bohai Bay and Laizhou Bay from the north to the south, respectively. Five sampling transects (28 seawater and 13 sediment sampling sites) representing the above three bays, the middle of the studied sea area and the boundary between the Bohai Sea and the Yellow Sea were set. Seawater and sediment sampling was carried out onboard of R/V *Dong Fang Hong 2*. According to the previous report (Filipovic et al., 2013), river inflow and wet deposition are considered as the dominant PFASs inputs to the sea. Due to the significant variation of precipitation in different seasons which may result in differences in river discharge into the ocean, the surface water and sediment samples were collected twice. They were collected in July 6 and November 21, 2013, representing the high-water and low-water periods, respectively. In total, 27 (in July) and 28 (in November) seawater samples and 13 sediment samples were collected.

Tianjin is the most industrialized, urbanized and populated city among the cities adjacent to the Chinese Bohai Sea. PFAS concentrations and compositions in wastewater and river water in Tianjin, which are directly discharged into Bohai Sea, were determined to investigate the sources of PFAS pollution in the Bohai Sea. Fifteen wastewater and river water samples were collected from rivers and drain outlets in Tianjin in July 6, 2013. Among them, 13 samples were mainly composed of river water and domestic sewage and only two (TJ10 and TJ12) samples of treated industrial wastewater.

One liter of seawater, one liter of wastewater, and 15 g of sediment were collected at each sampling site, using a stainless steel bucket and a grab sampler, respectively. The samples were stored in polypropylene containers. The water samples were stored at room temperature for less than a week prior to analysis, and the sediment

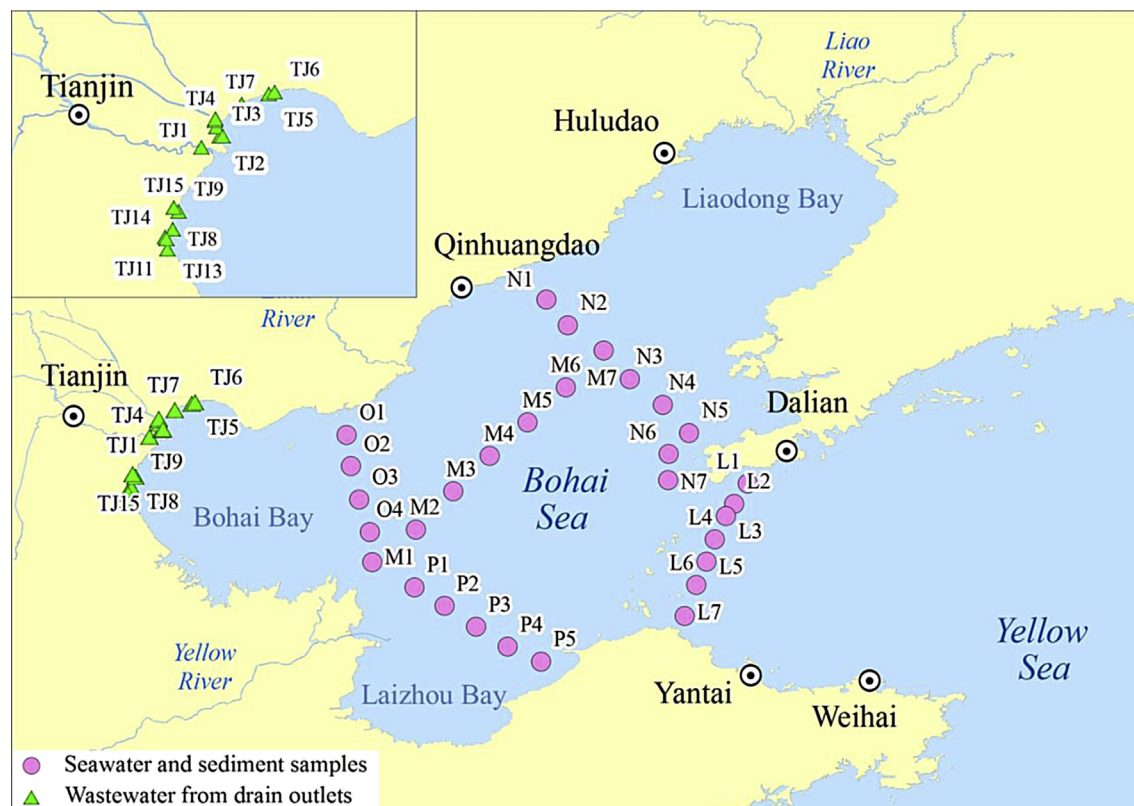


Fig. 1. Study area and sampling sites.

samples at $-20\text{ }^{\circ}\text{C}$ until analysis. To ensure that PFASs were not introduced as a result of background contamination, eight field blanks were prepared by containing cleaned Milli-Q water, carried to the sampling sites, and brought back to the laboratory with the water samples on each day when samples were collected. Prior to extraction, sediment samples were frozen-dried and ground before being homogenized by a porcelain mortar and pestle.

2.2. Materials

All isotopically labeled standards and native PFASs were purchased from Wellington Laboratories (Guelph, ON, Canada). Their abbreviations and purity are listed in Table S1. 19 PFASs including 13 PFCAs, 4 PFSA, FOSA and FOSAA were analyzed in this study. All analytes had matched stable isotope standards and they are also shown in Table S1. Methanol and methyl-*tert*-butyl ether (MTBE) were purchased from Tedia, USA. Tetrabutylammonium hydrogensulfate (TBAHS, HPLC grade) was purchased from Roe Scientific Inc. Milli-Q water was further treated using Waters Oasis HLB cartridges (200 mg, Milford, MA) to remove the potential PFAS

residues. All reagents were used as received.

2.3. Sample preparation and analysis

The water sample extraction method was adapted from a previously reported method (Bao et al., 2011; Chen et al., 2015). Briefly, 1000 mL of sample was filtered through a glass fiber filter ($1.6\text{ }\mu\text{m}$; Whatman, Florham Park, NJ) and then spiked with 2 ng of mass-labeled internal standards. Solid phase extraction (SPE) was conducted at a flow of 10 mL/min by a Sep-Pak concentrator (Waters Corp., Milford, MA). Waters Oasis HLB cartridges (200 mg, Milford, MA) were first conditioned with 10 mL of methanol and 10 mL of cleaned Milli-Q water. A 1000-mL aliquot of each water sample was then loaded onto the SPE cartridge. After the cartridges were dried completely by purging with high purity nitrogen, the target analytes were eluted from the cartridges with 2 mL of methanol at a flow rate of 1 mL/min. The extract was dried under a gentle stream of nitrogen, and then dissolved in 200 μL of methanol/10 mM ammonium acetate (40:60) to approximate the initial mobile-phase condition which was selected to separate PFASs in high

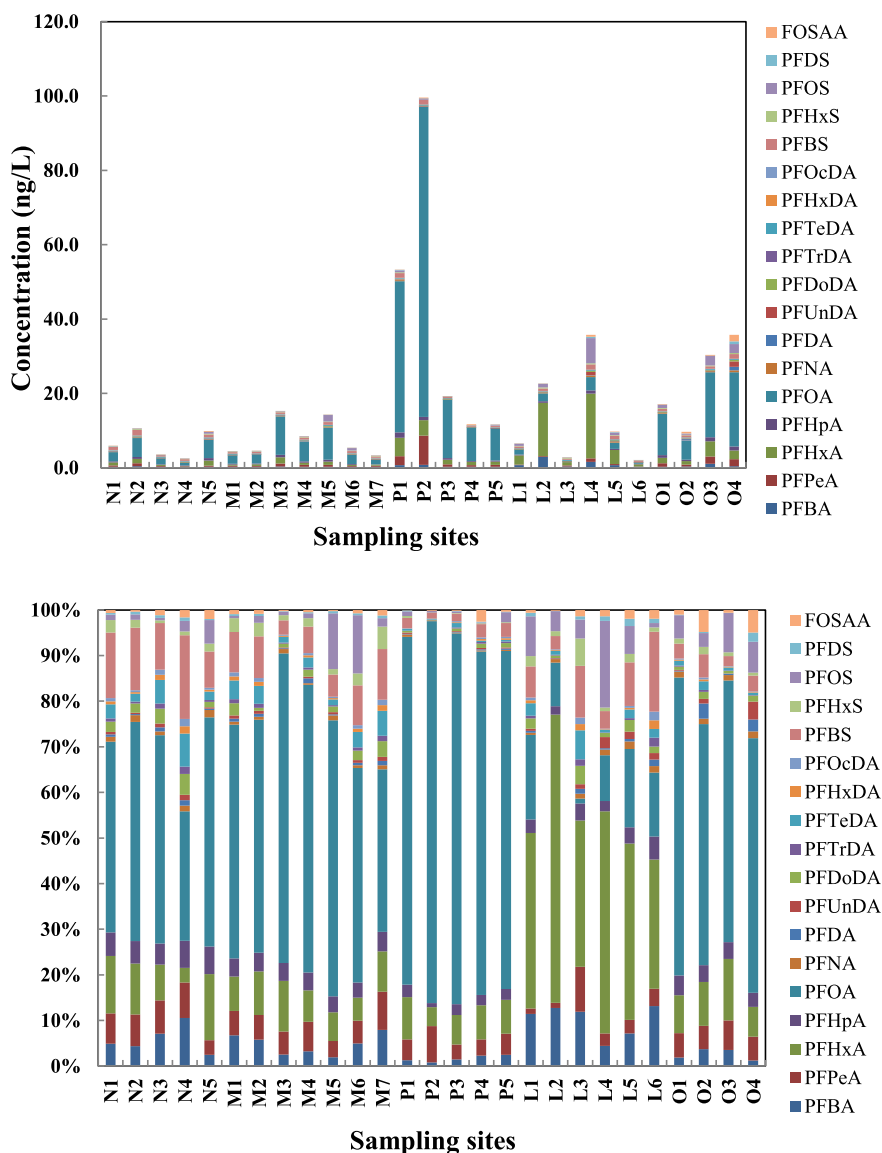


Fig. 2. Spatial distribution and composition of PFASs in seawater sampled in July (high-water period).

performance liquid chromatography system. The extracted sample was passed through a nylon filter (pore diameter 0.2 μm , Millipore, MA) and then transferred to a PP vial for instrumental analysis.

Sediment samples were frozen-dried and homogenized. They were then extracted using a method we previously reported (Chen et al., 2015). Briefly, five grams of sediment was transferred to a 50 mL PP centrifuge tube, and vortexed with 2 mL of cleaned Mill-Q water. 2 mL of 0.25 M Na_2CO_3 and 1 mL of 0.5 M tetrabutylammonium hydrogensulfate (TBAHS, HPLC grade) solutions were then added and vortex mixed before duplicate extraction with methyl *tert*-butyl ether (MTBE, HPLC grade). The combined MTBE extracts were brought to dryness under a gentle stream of high purity nitrogen, and reconstituted in a 1 mL mixture of methanol and 10 mM ammonium acetate (2:3, v/v) before final filtration with a 0.22 μm nylon filter. Prior to extraction, mass-labeled ISs (2 ng) were spiked into sediment samples.

PFASs analyses were accomplished using an Agilent 1200 high performance liquid chromatography system (Palo Alto, CA) coupled with an Agilent 6410 Triple Quadrupole (QQQ) mass spectrometer

(Santa Clara, CA). For each run, 10 μL of the sample was separated on an Agilent Eclipse Plus C18 column (2.1 \times 100 mm, 3.5 μm , Agilent, Palo Alto, CA). The mobile phase consisted of 10 mM ammonium acetate and methanol at a flow rate of 250 $\mu\text{L}/\text{min}$. The mobile phase gradient began at 40% methanol, was increased to 90% after 3 min, maintained for 17 min, increased to 100% methanol, and then maintained this level for 10 min. Finally, the gradient was returned to its initial conditions. The precursor and product ions were listed in Table S2.

2.4. Quality assurance and quality control

The method limit of quantification (MLQ) as the analyte peak required yielding a signal-to noise (S/N) ratio larger than 10:1. The MLQ values for each measured compound are shown in Table S2. One blank was performed for every batch of 10 samples. All of the measured compounds in the blanks were below their respective LODs. More information about the quality assurance and quality control is listed in the Supplementary materials.

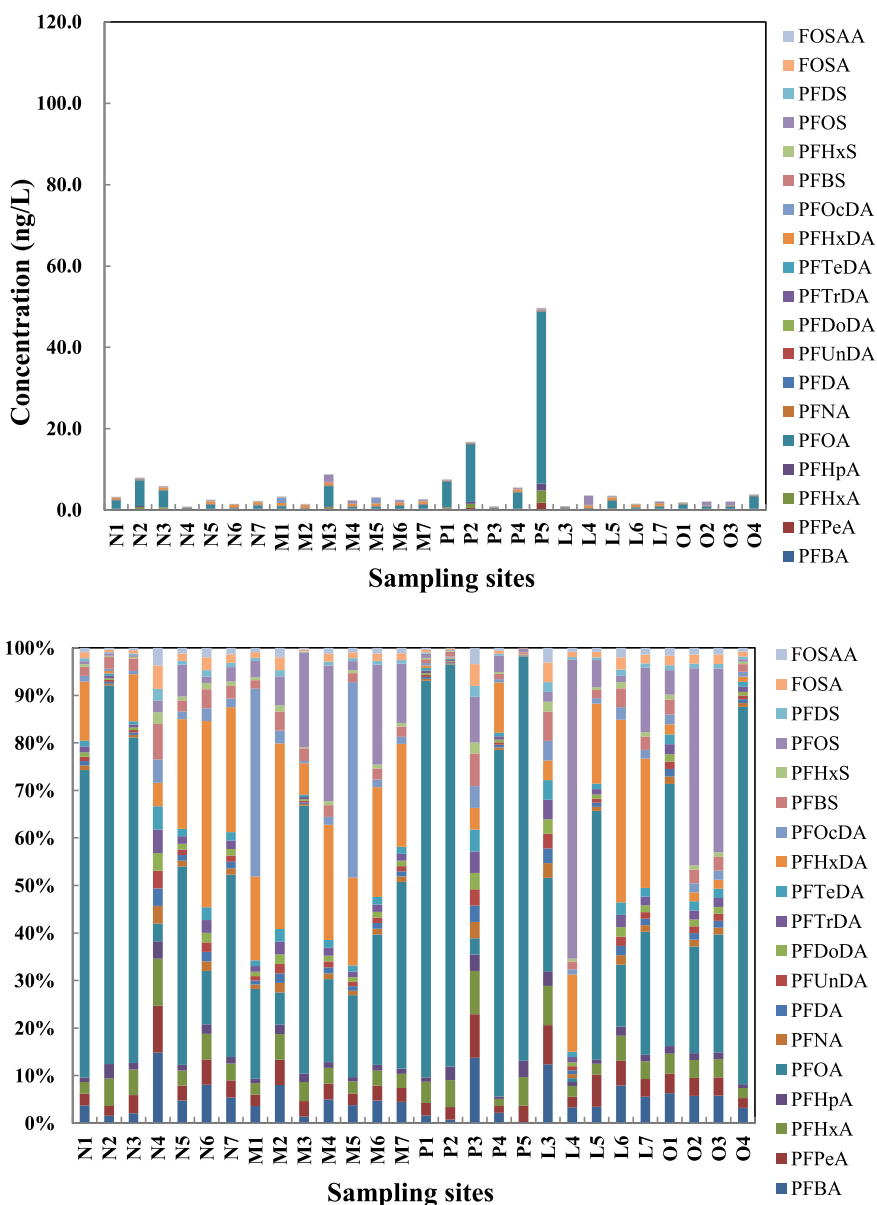


Fig. 3. Spatial distribution and composition of PFASs in seawater sampled in November (low-water period).

3. Results and discussion

3.1. PFASs in seawater from the Bohai Sea

PFAS concentrations and spatial distributions in seawater from the Bohai Sea are shown in Figs. 2 and 3. The concentration and detection frequency (*df*) of each compound are also shown in Table 1. At least one PFAS was detected in all seawater samples collected in July, while there were two seawater samples collected in November where PFAS concentrations were all below the detection limits. The concentrations of total PFASs in the seawater samples from the Bohai Sea ranged from <MLQ to 99.4 ng/L.

As shown in Figs. 2 and 3, total concentrations, dominant compounds and the spatial distributions of PFASs in seawater sampled in high-water period and low-water period were observed different. In samples collected in July, 11 of the target compounds (C4–C9, C12 and C14 PFCAs, as well as C4–C6 PFASs) were measured at concentrations exceeding the MLQ in more than half of the samples (Table 1, *df* ≥ 50%), whereas only three pollutants (PFOA, PFHxDA and PFOS) were detected with *df* ≥ 50% in samples collected in November. The total PFAS concentrations in seawater sampled in July ranged from 1.65 to 99.4 ng/L, with a median of 9.78 ng/L and an average of 16.7 ng/L, and in November, from <MLQ to 48.9 ng/L, with a median of 1.60 ng/L and an average of 4.44 ng/L. It was found that both of the detection frequencies and the total PFAS levels in seawater sampled in July (high-water period) were much higher than those in November (low-water period). According to the previous studies (Boulangier et al., 2005; Filipovic et al., 2013), river inflow and atmospheric deposition (wet deposition which is related to the precipitation) are the dominant inputs of PFASs in the sea and lake. Meanwhile, wastewater effluents in the studied area are continuously discharged into the sea. It is suggested that the differences of *df* and levels for PFASs in the Bohai Sea in different seasons are mainly due to the differences in rainfall runoff and thus riverine input, and also the wet deposition of PFASs into the ocean.

In terms of level for each target compound, high concentrations of PFOA (median 4.97 ng/L), PFHxA (median 0.93 ng/L) and PFBS (median 0.49 ng/L) were found in seawater samples collected in July, accounting for 47%, 16% and 7% of the total PFASs on average, respectively (see Fig. 4). For seawater samples collected in

November, PFOA, PFOS and PFHxDA were dominant with median concentrations of 0.86, 0.10 and 0.59 ng/L, which accounted for an average of 40%, 14% and 11%, respectively. By comparing the patterns of dominant compounds in different sampling time, seasonal variation was observed, indicating that the dominant sources of PFASs emitted into the Bohai Sea are seasonally different. Overall, PFOA was the most prevalent PFAS in the seawater from Bohai Sea. This result is consistent with many earlier reports (Chen et al., 2011; Gao et al., 2014) in which PFOA is considered the most industrially utilized PFAS and the most abundant PFAS in the Bohai Sea.

In the Bohai Sea, the highest total PFASs concentration in seawater sampled in July was 99.4 ng/L at site P2, which is close to Laizhou Bay. Generally, concentrations of PFASs should decrease from the nearshore locations to the open waters if the seawater exchange is well. However, this phenomenon of decreasing PFAS concentrations from the coastal area to the open waters was not found in this area. In different sampling transects in July, the highest PFAS concentrations were 10.7, 15.3, 99.6, 35.8 and 36.0 ng/L at N2, M3, P2, L4 and O4 sites, respectively. In November, the highest total PFASs concentration were found to be 7.9, 8.8, 49.7, 3.6, 3.8 ng/L at N2, M3, P5, L4 and O4 sites, respectively, which are the same sites as in July except the P sampling transect. It was found that neither the sampling sites where the total PFAS concentrations are the highest in July nor that in November were the closest to the shore. The decreasing concentration of PFASs from the coastal to the open waters was not observed. This may be due to that the Bohai Sea is semi-enclosed, which results in the limited exchanges of the seawater. Nevertheless, spatial trends of PFASs between different sampling transects were found. In seawater sampled in July, the highest and lowest PFAS concentration level ranges were found at P and O sampling transects, respectively. From Figs. 2 and 3, it was shown that PFAS pollution in Laizhou Bay was the most serious. This accords with the results from the other report (Gao et al., 2014) in which PFAS in marine sediments from this area was investigated.

A comparative analysis was conducted between the Bohai Sea and other sea areas in the world regarding the concentrations of the total measured PFASs in seawater samples (Fig. 5). It was shown that the total PFASs concentration range observed in this study was moderate among the compared regions. The concentrations in this work were lower than those from estuarine and coastal areas of

Table 1
Concentrations (ng/L) and detection frequencies (*df*) of PFASs in seawater sampled in high-water and low-water periods.

Compounds	Sampling in July				Sampling in November			
	Range	Median	Mean	<i>df</i> (%)	Range	Median	Mean	<i>df</i> (%)
PFBA	0.25–2.90	0.30	0.54	100	<MLQ	<MLQ	<MLQ	0
PFPeA	<MLQ–7.91	0.43	0.88	93	<MLQ–1.70	<MLQ	0.17	26
PFHxA	0.10–17.4	0.93	2.54	96	<MLQ–2.97	<MLQ	0.10	22
PFHpA	0.11–1.46	0.35	0.46	100	<MLQ–1.70	<MLQ	0.10	22
PFOA	<MLQ–83.4	4.97	9.90	96	<MLQ–42.3	0.86	3.62	89
PFNA	<MLQ–0.53	0.06	0.12	52	<MLQ	<MLQ	<MLQ	0
PFDA	<MLQ–0.93	0.03	0.08	26	<MLQ	<MLQ	<MLQ	0
PFUnDA	<MLQ–1.40	<MLQ	0.11	22	<MLQ	<MLQ	<MLQ	0
PFDoDA	<MLQ–0.46	0.12	0.16	93	<MLQ	<MLQ	<MLQ	0
PFTTrDA	<MLQ	<MLQ	<MLQ	0	<MLQ	<MLQ	<MLQ	0
PFTeDA	<MLQ–0.21	0.18	0.19	89	<MLQ	<MLQ	<MLQ	0
PFHxDA	<MLQ	<MLQ	<MLQ	0	<MLQ–0.59	0.59	0.38	59
PFOcDA	<MLQ	<MLQ	<MLQ	0	<MLQ–1.32	<MLQ	0.09	7
PFBS	0.32–1.46	0.49	0.66	100	<MLQ–0.24	<MLQ	<MLQ	19
PFHxS	0.14–0.28	0.17	0.18	74	<MLQ	<MLQ	<MLQ	0
PFOS	<MLQ–6.80	0.25	0.74	85	<MLQ–2.27	0.10	0.34	82
PFDS	<MLQ–0.71	0.05	0.13	26	<MLQ	<MLQ	<MLQ	0
FOSAA	<MLQ–1.78	0.20	0.44	33	<MLQ	<MLQ	<MLQ	0
FOSA	<MLQ–0.25	<MLQ	<MLQ	7	<MLQ	<MLQ	<MLQ	0
PFASs	1.65–99.4	9.78	16.7	100	<MLQ–48.9	1.60	4.44	93

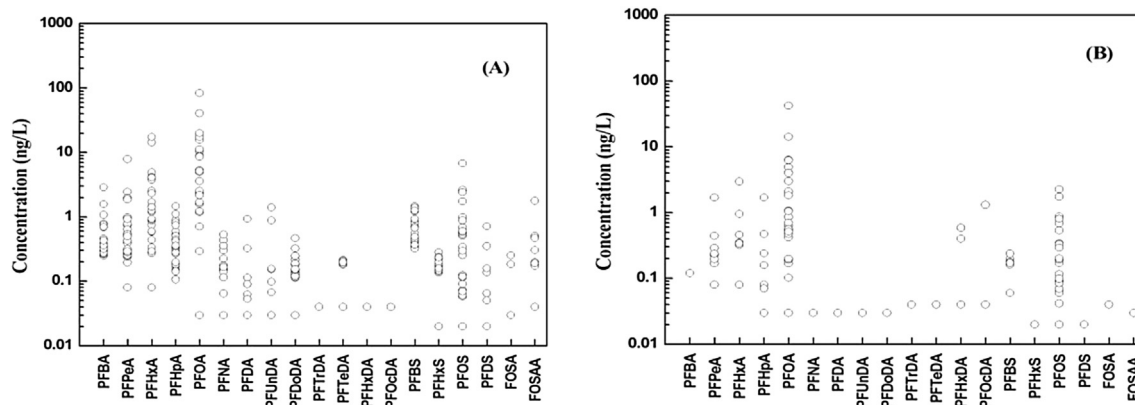


Fig. 4. PFAS concentrations in the seawater samples of Bohai Sea in July (A) and November (B).

Korea (Naile et al., 2010), Tokyo Bay basin of Japan (Zushi et al., 2011) and Liaodong Bay basin of China (Chen et al., 2015), but higher than those from Sydney Harbour of Australia (Thompson et al., 2011), Tokyo Bay of Japan (Ahrens et al., 2010b) and marine environment of Hong Kong (Loi et al., 2013).

3.2. PFASs in wastewater and river water from Tianjin drain outlets

Drain outlets in this study is a general concept, including riverine discharge and coastal wastewater discharge directly into the Bohai Sea. This is one of the dominant sources of PFASs in marine environment, and the other one is atmospheric deposition based on the results from Filipovic et al. (2013). To investigate the current pollution status in drain outlets and its potential contribution to PFAS pollution in the sea, PFASs were quantified in the collected effluents from 15 drain outlets in Tianjin. These 15 drain outlets include ten river outfalls, three effluent emissions from wastewater treatment plants, and two treated industrial wastewater discharge from industrial zone or plants. C4–C12 PFCAs and C4, C6, C8, and C10 PFASs were detected in all effluent samples. The

total PFAS concentrations were calculated. As shown in Fig. 6, the concentrations of PFASs ranged from 103 ng/L to 443 ng/L. The highest total PFASs concentration was four times higher than that in seawater from Bohai Sea (99.4 ng/L). It could be observed that direct discharge of wastewater from drain outlets was responsible for the contamination of PFASs in Bohai Sea area. Variation in the patterns of dominant compounds was observed between different kinds of drain outlets. PFHxS and PFOA were dominant in the samples from industrial drain outlets (sites TJ10 and TJ12), while PFHxA and PFOA were dominant in the other ten samples from rivers and municipal drain outlets. However, only two industrial wastewater samples were included in this study. It was worthy to note that this observed different dominant PFAS patterns were limited to the drain outlets investigated in this study. Moreover, the prevalent compounds (PFOA and PFHxA) in rivers and municipal drain outlets were consistent with those in seawater, but their median concentrations (PFOA: 101.4 ng/L; PFHxA: 21.5 ng/L) were much higher than those in seawater samples from the Bohai Sea, with PFOA and PFHxA median concentrations of 4.97 and 0.93 ng/L, respectively. This indicated that wastewater from drain outlets was a main contamination source of PFOA and PFHxA in the Bohai Sea.

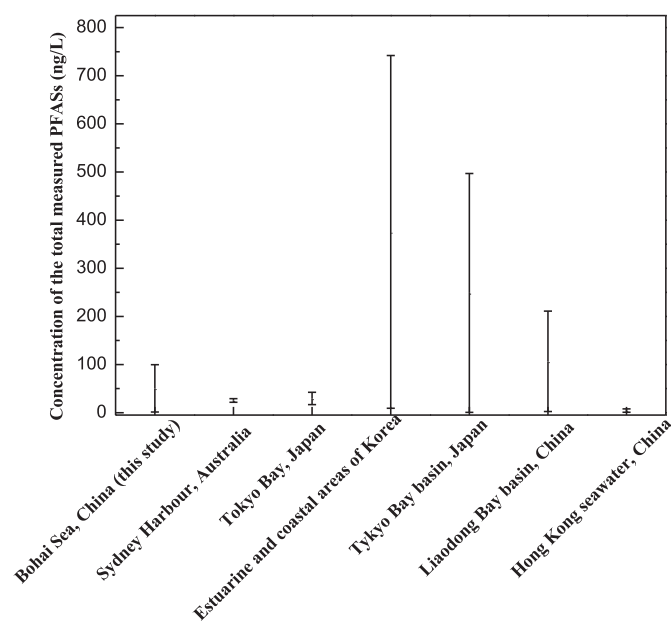


Fig. 5. Comparison of the total concentration ranges of PFASs (ng/L) in water samples with previous reports in other areas.

3.3. Spatial distributions and levels of PFASs in surface sediments

Thirteen surface sediment samples collected from Bohai Sea in July and November were analyzed. PFASs concentration range, median and mean concentration, together with their detection frequencies (*df*) are presented in Table 2. As shown in Table 2, for sediment samples collected in July, PFOA, PFDA, PFUnDA, PFDoDA, PFHxDA, PFOcDA, PFBS and PFOS were detected in all samples, whereas the detection frequencies for C4–C7 PFAAs, and FOSA were 0. In November, PFDoDA (92%) and PFOS (85%) were not fully detected in sediment samples compared with *dfs* in July. The concentrations of total PFASs in surface sediments ranged from 0.50 to 2.78 ng/g dw and from 0.33 to 1.75 ng/g dw, with the median concentrations of 0.73 and 0.61 ng/g dw in July and November, respectively. This total PFASs concentration in sediment in July was comparable to that in November, indicating that the seasonal variation in total PFAS concentrations were not significant. In other words, the total PFAS concentration in sediment samples was less seasonally sensitive than those in seawater samples in marine environment. Previous reports (Higgins and Luthy, 2006; Chen et al., 2012a) indicated that sorption of PFASs would reach equilibrium before 48 h. This equilibrium time is relatively short as compared with the seasonal variation time, and thus this may not be the factor influencing the above less seasonally sensitivity for

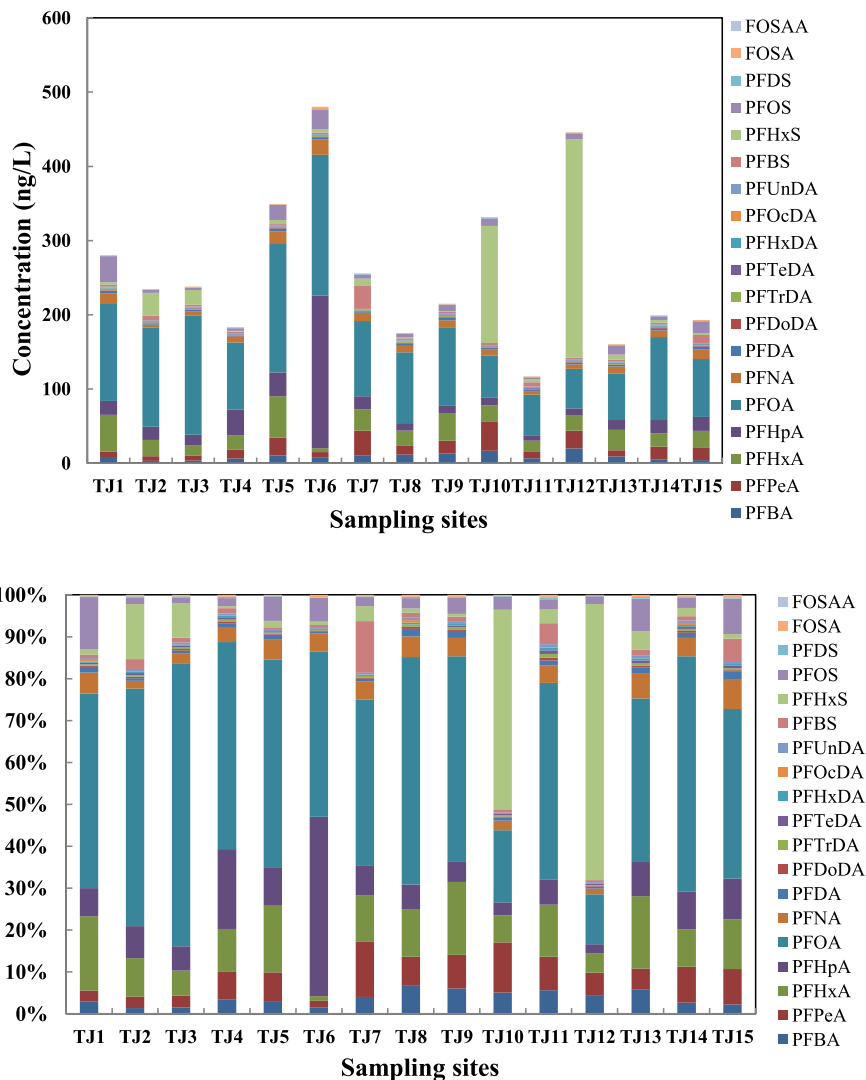


Fig. 6. Spatial distribution and composition of PFASs sampled in drain outlets from Tianjin, China.

Table 2
Concentrations (ng/g dw) and detection frequencies (df) of PFASs in sediment.

Compounds	Sampling in July				Sampling in November			
	Range	Median	Mean	df (%)	Range	Median	Mean	df (%)
PFBA	<MLQ	<MLQ	<MLQ	0	<MLQ	<MLQ	<MLQ	0
PFPeA	<MLQ	<MLQ	<MLQ	0	<MLQ	<MLQ	<MLQ	0
PFHxA	<MLQ	<MLQ	<MLQ	0	<MLQ	<MLQ	<MLQ	0
PFHpA	<MLQ	<MLQ	<MLQ	0	<MLQ-0.18	0.14	0.14	15
PFOA	0.11–0.81	0.24	0.29	100	0.08–0.64	0.28	0.30	100
PFNA	<MLQ–0.16	<MLQ	0.09	46	<MLQ-0.15	<MLQ	0.08	31
PFDA	0.02–0.03	0.02	0.02	100	0.02–0.03	0.02	0.02	100
PFUnDA	0.02–0.03	0.02	0.03	100	0.02–0.04	0.02	0.03	100
PFDODA	0.03–0.05	0.03	0.03	100	<MLQ-0.04	0.03	0.03	92
PFTrDA	<MLQ–0.05	<MLQ	0.04	38	<MLQ-0.04	<MLQ	<MLQ	15
PFTeDA	<MLQ-0.04	<MLQ	<MLQ	31	<MLQ-0.04	<MLQ	<MLQ	23
PFHxDA	0.06–0.07	0.07	0.07	100	0.06–0.07	0.07	0.07	100
PFOcDA	0.07–0.12	0.07	0.08	100	0.07–0.08	0.07	0.07	100
PFBS	0.04–0.19	0.05	0.06	100	0.05–0.09	0.05	0.06	100
PFHxS	<MLQ–0.09	0.03	0.03	77	<MLQ-0.03	<MLQ	<MLQ	31
PFOS	0.02–0.74	0.04	0.11	100	<MLQ-0.14	0.06	0.06	85
PFDS	<MLQ-0.10	0.03	0.04	54	<MLQ-0.22	<MLQ	0.08	38
FOSAA	<MLQ-0.66	0.21	0.29	62	<MLQ-0.37	<MLQ	0.16	46
FOSA	<MLQ	<MLQ	<MLQ	0	<MLQ	<MLQ	<MLQ	0
PFASs	0.50–2.78	0.73	0.98	100	0.33–1.75	0.61	0.72	100

PFAS concentrations in marine sediment samples. The deposition rate for coastal marine sediment ranged at hundreds of mm per one thousand years, indicating that sediment monitoring could be considered as an indicator of PFAS concentrations cumulated through time while water monitoring is a punctual measure. This was speculated as the reason why PFAS concentration in sediment samples is less sensitive than those in seawater samples. The total PFASs concentration range in Bohai Sea investigated in this study was comparable to those in previous reports from coastal regions of the northern Bohai Sea in China (ND–4.3 ng/g dw, [Chen et al., 2011](#)), Chinese Bohai Sea (0.06–2.98 ng/g dw, [Gao et al., 2014](#)), and Hong Kong marine sediment (0.10–1.59 ng/g dw, [Loi et al., 2013](#)). However, it was higher than that from the coastal areas of Korea (<2 ng/g dw, [Naile et al., 2010](#)), Tokyo Bay in Japan (0.29–0.36 ng/g dw, [Ahrens et al., 2010b](#)) and the Cantabrian Sea in North Spain (0.01–0.13 ng/g dw, [Gomez et al., 2011](#)).

Composition of PFASs in each sampling site in July and November is shown in [Figs. 7 and 8](#), respectively. PFOA was the most abundant PFASs in sediments collected both in July and November with levels ranging from 0.11 to 0.81 ng/L and from 0.08 to 0.64 ng/L, accounting for 30% and 40% of the total PFASs on average in July and November, respectively. The second most abundant PFAS was PFOcDA, accounting for an average of 10% and 11% in July and November, respectively. No variation in composition of PFASs between different times was observed. The PFASs with carbon length above 10 were more frequently detected in sediments than in seawater samples. This observation was reasonable because PFASs having more fluorinated carbons are more hydrophobic, which results in different sorption capability of such PFASs by sediment ([Ahrens et al., 2009](#); [Higgins and Luthy, 2006](#)).

As shown in [Figs. 7 and 8](#), the total PFASs concentrations in O3 sampling site were the highest for both sediment samples

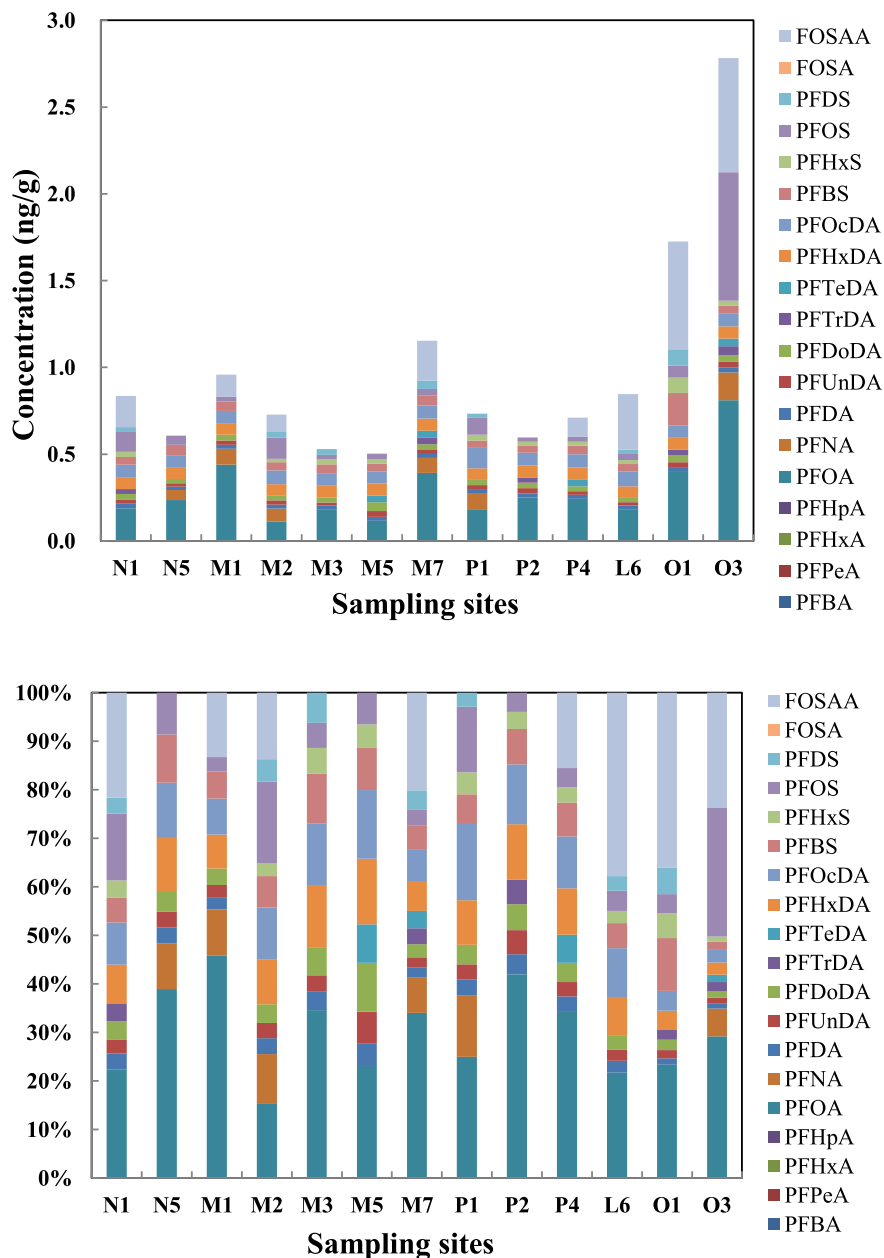


Fig. 7. Spatial distribution and composition of PFASs in sediments sampled in July.

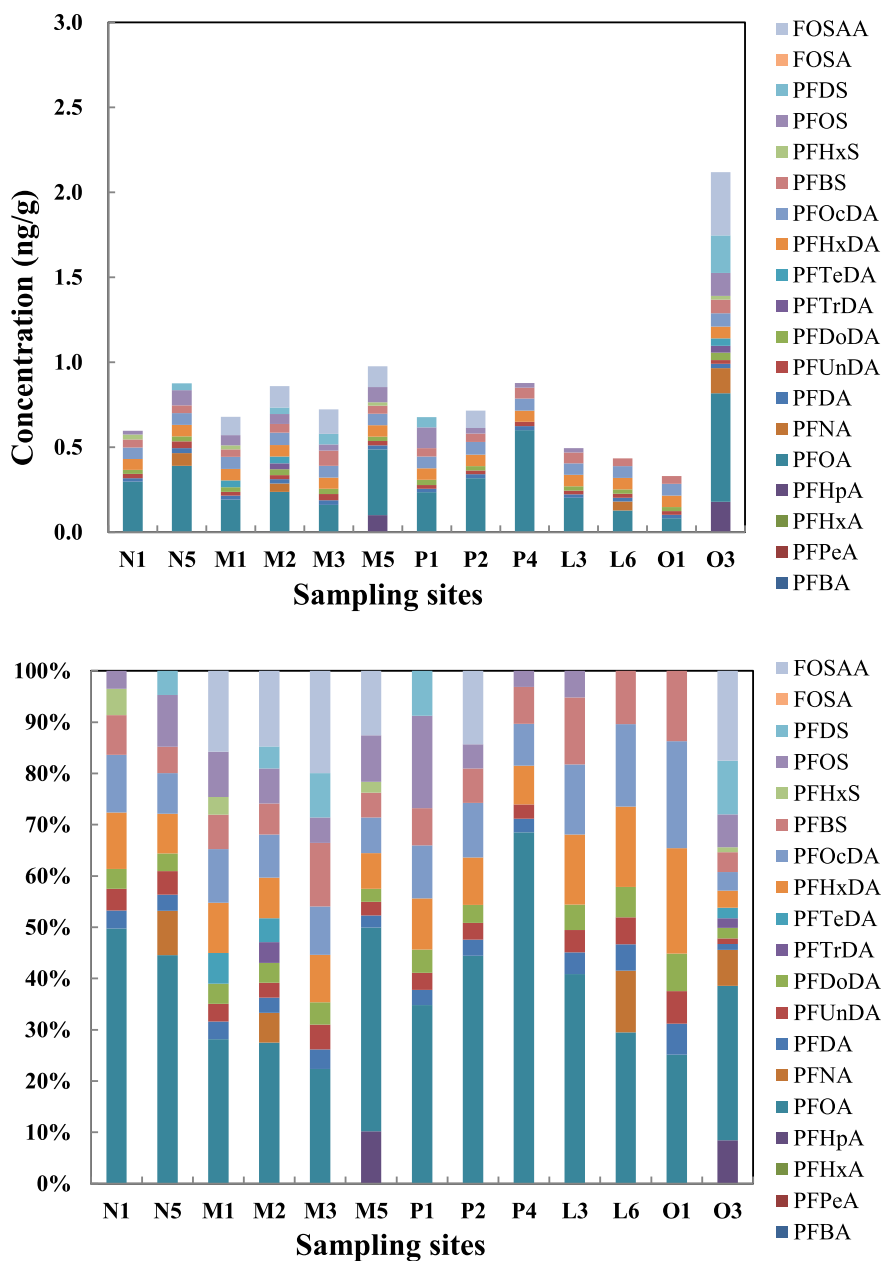


Fig. 8. Spatial distribution and composition of PFASs in sediments sampled in November.

collected in July and November, whereas they were not significantly various in other sites. O3 sampling site was located in the middle of the sampling transect for Bohai Bay. The cities along the Bohai Bay were more industrialized and populated than the other two bays (Liaodong Bay and Laizhou Bay) in the Bohai Sea. This may result in the high mass load of PFASs into the Bohai Sea and the high concentration of PFASs in sediment samples in this sampling transect. No spatial trends of PFASs were found among the sampling transects and from the nearshore locations to the open waters. This is in agreement with the results in previous study (Gao et al., 2014). In addition, the spatial distribution of the total PFASs concentration in sediments in July was found to be similar to that in November.

4. Conclusion

This paper presents the first comprehensive spatial and

seasonal survey of PFASs pollution in seawater and sediment from the total Bohai Sea, China, which is a rapidly urbanized and semi-enclosed sea for China. PFAS concentrations in seawater sampled in high-water period (July) were much higher than those sampled in low-water period (November), whereas their concentrations didn't show seasonal variation in sediment. PFOA was the dominant compound in both of seawater and sediment. Among three bays in Chinese Bohai Sea, PFAS pollution in seawater from Laizhou Bay was the most serious. Overall PFASs concentrations in this study region were moderate based on the comparison with those in other areas. PFASs concentrations in river water and wastewater from drain outlets of Tianjin, the most industrialized and populated city along the Bohai Sea, showed that the highest PFASs concentration was 4 times higher than that in seawater from Bohai Sea and suggested that water from drain outlets might be a significant source of PFAS pollution in this area.

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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.2016.05.017>.

References

- Ahrens, L., Yamashita, N., Yeung, L.W.Y., Taniyasu, S., Horii, Y., Lam, P.K.S., Ebinghaus, R., 2009. Partitioning behavior of per- and polyfluoroalkyl compounds between pore water and sediment in two sediment cores from Tokyo Bay. *Jpn. Environ. Sci. Technol.* 43, 6969–6975.
- Ahrens, L., Xie, Z., Ebinghaus, R., 2010a. Distribution of perfluoroalkyl compounds in seawater from northern Europe, Atlantic Ocean, and Southern Ocean. *Chemosphere* 78, 1011–1016.
- Ahrens, L., Taniyasu, S., Yeung, L.W.Y., Yamashita, N., Lam, P.K.S., Ebinghaus, R., 2010b. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. *Chemosphere* 79, 266–272.
- Bao, J., Liu, W., Liu, L., Jin, Y., Dai, J., Ran, X., Zhang, Z., Tsuda, S., 2011. Perfluorinated compounds in the environment and the blood of residents living near fluorochemical plants in Fuxin, China. *Environ. Sci. Technol.* 45 (19), 8075–8080.
- Boulanger, B., Peck, A.M., Schnoor, J.L., Hornbuckle, K.C., 2005. Mass budget of perfluorooctane surfactants in Lake Ontario. *Environ. Sci. Technol.* 39, 74–79.
- Chen, C., Wang, T., Khim, J.S., Luo, W., Jiao, W., Lu, Y., Naile, J.E., Hu, W., Zhang, X., Geng, J., Bi, C., Li, J., Giesy, J.P., 2011. Perfluorinated compounds in water and sediment from coastal regions of the northern Bohai Sea, China. *Chem. Ecol.* 27, 165–176.
- Chen, H., Zhang, C., Yu, Y., Han, J., 2012a. Sorption of perfluorooctane sulfonate (PFOS) on marine sediments. *Mar. Pollut. Bull.* 64, 902–906.
- Chen, H., Zhang, C., Han, J., Yu, Y., Zhang, P., 2012b. PFOS and PFOA in influents, effluents, and biosolids of Chinese wastewater treatment plants and effluent-receiving marine environments. *Environ. Pollut.* 170, 26–31.
- Chen, H., Zhang, C., Han, J., Sun, R., Kong, X., Wang, X., He, X., 2015. Levels and spatial distribution of perfluoroalkyl substances in China Liaodong Bay basin with concentrated fluorine industry parks. *Mar. Pollut. Bull.* 2, 965–971.
- Filipovic, M., Berger, U., McLachlan, M.S., 2013. Mass balance of perfluoroalkyl acids in the Baltic Sea. *Environ. Sci. Technol.* 47, 4088–4095.
- Gao, Y., Fu, J., Zeng, L., Li, A., Li, H., Zhu, N., Liu, R., Liu, A., Wang, Y., Jiang, G., 2014. Occurrence and fate of perfluoroalkyl substances in marine sediments from the Chinese Bohai sea, Yellow sea, and east China sea. *Environ. Pollut.* 194, 60–68.
- Gomez, C., Vicente, J., Echavarri-Erasun, B., Porte, C., Lacorte, S., 2011. Occurrence of perfluorinated compounds in water, sediment and mussels from the Cantabrian Sea (North Spain). *Mar. Pollut. Bull.* 62, 948–955.
- Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* 40, 7251–7256.
- Kelly, B.C., Ikononou, M.G., Blair, J.D., Surridge, B., Hoover, D., Grace, R., Gobas, F.A.P.C., 2009. Perfluoroalkyl contaminants in an arctic marine food web: trophic magnification and wildlife exposure. *Environ. Sci. Technol.* 43, 4037–4043.
- Lau, C., 2012. Perfluorinated compounds. *EXS* 101, 47–86.
- Li, J., Guo, F., Wang, Y., Zhong, Y., Zhao, Y., Wu, Y., 2013. Can nail, hair and urine be used for biomonitoring of human exposure to perfluorooctane sulfonate and perfluorooctanoic acid? *Environ. Int.* 53, 47–52.
- Lindstrom, A.B., Strynar, M.J., Libelo, E.L., 2011. Polyfluorinated compounds: past, present, and future. *Environ. Sci. Technol.* 45 (19), 7954–7961.
- Loi, E.I.H., Yeung, L.W.Y., Mabury, S.A., Lam, P.K.S., 2013. Detections of commercial fluorosurfactants in Hong Kong marine environment and human blood: a pilot study. *Environ. Sci. Technol.* 47, 4677–4685.
- Naile, J.E., Khim, J.S., Wang, T., Chen, C., Luo, W., Kwon, B., Park, J., Koh, C., Jones, P.D., Lu, Y., Giesy, J.P., 2010. Perfluorinated compounds in water, sediment, soil and biota from estuarine and coastal areas of Korea. *Environ. Pollut.* 158, 1237–1244.
- Post, G.B., Cohn, P.D., Cooper, K.R., 2012. Perfluorooctanoic acid (PFOA), an emerging drinking water contaminant: a critical review of recent literature. *Environ. Res.* 116, 93–117.
- Thompson, J., Roach, A., Eaglesham, G., Bartkow, M.E., Edge, K., Mueller, J.F., 2011. Perfluorinated alkyl acids in water, sediment and wildlife from Sydney Harbour and surroundings. *Mar. Pollut. Bull.* 62, 2869–2875.
- Wang, J.S., Li, Y., Liu, Y., Zhang, H.X., Dai, J.Y., 2010. Disturbance of perfluorooctanoic acid on development and behavior in *Drosophila* Larvae. *Environ. Toxicol. Chem.* 29, 2117–2122.
- Zushi, Y., Ye, F., Motegi, M., Nojiri, K., Hosono, S., Suzuki, T., Kosugi, Y., Yaguchi, K., Masunaga, S., 2011. Spatially detailed survey on pollution by multiple perfluorinated compounds in the Tokyo Bay basin of Japan. *Environ. Sci. Technol.* 45 (7), 2887–2893.