



Perfluoroalkyl acids (PFAAs) in riverine and coastal sediments of Laizhou Bay, North China

Zhen Zhao^{a,b,d}, Jianhui Tang^{a,*}, Zhiyong Xie^b, Yingjun Chen^a, Xiaohui Pan^a, Guangcai Zhong^{a,b}, Renate Sturm^b, Gan Zhang^c, Ralf Ebinghaus^b

^a Key Laboratory of Coastal Zone Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, CAS, Yantai 264003, PR China

^b Department for Environmental Chemistry, Institute of Coastal Research, Centre for Materials and Coastal Research, Helmholtz-Zentrum Geesthacht, Geesthacht, Germany

^c State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, CAS, Guangzhou 510640, PR China

^d University of Chinese Academy of Sciences, Beijing 100049, PR China

HIGHLIGHTS

- ▶ Perfluoroalkyl acids are systematically investigated in the riverine and coastal sediments.
- ▶ PFOA is the dominant compounds.
- ▶ Distribution patterns of PFOA in river sites are determined by sources.
- ▶ Hydrological processes play a major role on the distribution of PFOA in coastal sediment.
- ▶ Risk assessment showed negligible effects of PFASs to benthic organism.

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ABSTRACT

This study investigates the concentrations and distributions of perfluoroalkyl acids (PFAAs), including perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulphonates (PFASs), in surface sediments from Laizhou Bay and its adjacent rivers. \sum PFAAs showed much higher levels in the river sediment (with a mean of 5.25 ng/g dw) than in the coastal sediment (with a mean of 0.76 ng/g dw). Perfluorooctanoic acid (PFOA) was the predominant compound, accounting for 50% to 97% of \sum PFAA concentrations in 70% of the samples. The highest concentrations were detected in the Xiaoqing River, possibly due to the rapid development of the nearby fluorochemical industry. Hydrodynamics strongly influenced the distribution of PFAAs in Laizhou Bay. The hydrophilic property of shorter-chained PFAAs ($C \leq 8$) allowed them to be transported to the inner bay via currents, to adsorb onto suspended sediment and then to be deposited. The Xiaoqing River showed the highest PFOA concentration (76.9 ng/g dw) among the bodies of sediment that had been studied worldwide, which might pose a potential threat for the benthic organisms of this river.

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1. Introduction

Perfluoroalkyl acids (PFAAs) have been produced and used as surfactants and surface protectors for more than five decades (OECD, 2002). These compounds are widely applied in textile coatings, paper packaging, fire-fighting foams, insecticides, and fluoropolymer manufacturing worldwide (Key et al., 1997; Paul et al., 2008; Prevedouros et al., 2005). The perfluoroalkyl chains and polar head groups of PFAAs imbue the chemicals with both hydrophobic and hydrophilic properties (Kissa, 2001). PFAAs were detected in various environmental matrices, including air (Dreyer et al., 2009; Li et al., 2011b),

environmental and tap water (Ahrens, 2011; Bao et al., 2012; Yamashita et al., 2005), sediment (Higgins et al., 2005) and human blood (Kannan et al., 2004). Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) were frequently detected in water and sediments due to their various direct and indirect sources (Paul et al., 2008; Prevedouros et al., 2005) and potential for long-range transport (LRT) via marine currents (Ahrens et al., 2009a; Nash et al., 2010). According to toxicological studies, PFOS could cause acute to chronic toxicity in freshwater fish and liver and thyroid cancer in rats, and PFOA caused acute toxicity in invertebrates and is related to liver, pancreatic, and testicular tumours in laboratory animals (Andersen et al., 2008; Hekster et al., 2003).

Sediments had been investigated in China (Bao et al., 2010a), Japan (Ahrens et al., 2009b), the United States (Senthil et al., 2009), Germany (Becker et al., 2008), France (Labadie and Chevreuil,

* Corresponding author. Tel.: +86 535 2109151; fax: +86 535 2109000.

E-mail address: jhtang@yic.ac.cn (J. Tang).

2011), Spain (Gomez et al., 2011) and Australia (Thompson et al., 2011) as an important sink and reservoir of PFAAs. Previous studies had suggested levels of tens to hundreds of ng/g for PFOA and PFOS in riverine and coastal sediments (Table 1). The highest concentrations of PFOS and PFOA in riverine sediments in China were detected in the Yangtze River estuary (536.7 ng/g dw) and in the Xi River, Liaoning Province (48 ng/g dw), respectively (Bao et al., 2009, 2010a). High levels of these substances had been attributed to rapid urbanisation and the development of the fluorochemical industry. Several factors influence the distribution of PFAAs in the coastal environment, including the partitioning behaviours between sediment and water (Higgins and Luthy, 2006), meteorology controlling the movement of volatile compounds (Dreyer et al., 2009), hydrological conditions affecting the transportation of the compounds in water (Ahrens et al., 2009a), and the dependence of bioaccumulation on the chain lengths of PFAAs (Martin et al., 2003). Industrial parks (Rumsby et al., 2009), waste water treatment plants (Sinclair and Kannan, 2006; Xiao et al., 2012) and accidental spills of PFAA-containing products (Awad et al., 2011) are potential point sources for PFAAs.

Laizhou Bay is part of the Bohai Sea and has an area of approximately 4600 km². The most important discharge river for the bay is the Yellow River, which had discharged approximately 12.7×10^8 t/a sediment into the Bohai Sea from 1919 to 2008 (Mu et al., 2012). The rapid urbanisation and industrialisation in the adjacent area had resulted in the rapid deterioration of the local environmental quality. The levels of organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), and polychlorinated naphthalenes (PCNs) in the sediments of the Laizhou Bay and its adjacent rivers had been investigated by Zhong et al. (2011) and Pan et al. (2011a, 2011b). Sediment samples in rivers/ditches near an industrial park had been shown to contain relatively high concentrations of PBDEs, hexachlorocyclohexanes (HCHs), and PCNs compared to other regions. This study aims to reveal the spatial distribution of PFAAs in sediments from the Laizhou Bay and its adjacent rivers, extrapolate the distribution dynamics, and assess the risk these compounds pose to local ecosystem.

2. Material and methods

2.1. Chemical and reagent

A mixture of fifteen PFAAs, (i.e. C₄-, C₆–C₈- and C₁₀-PFSAs and C₄–C₁₄-PFCAs), and nine mass labelled standards, (i.e. ¹³C labelled C₄-, C₆-, C₈–C₁₂-PFCAs and C₈-PFSAs and ¹⁸O labelled C₆-PFSAs) (Tables 2S and 3S) were purchased from Wellington Laboratories. Methanol (Suprasolv grade), ammonium hydroxide (25%, Suprapur), sodium hydroxide and hydrochloric acid were purchased from Merck (Darmstadt, Germany). Millipore water was produced by a Milli-Q Plus 185 system (Zug, Germany).

2.2. Sampling

The general information of Laizhou Bay and its adjacent region was introduced by Pan et al. (2011a, 2011b). Twenty-six surface (0–10 cm) coastal sediment samples and twenty-four river sediment samples were collected in September and October, 2009, in Laizhou Bay and its adjacent rivers using a stainless steel grab sampler. The locations of the sampling sites were shown in Fig. 1, and the general characteristics of the sites were presented in Table S3. The sediment samples were stored in brown jars, which were pre-cleaned using methanol and deionised water, and stored at –20 °C before being freeze-dried. After the sediment samples were freeze-dried for 72 h, the sediments were homogenised by agate mortar and pestle, and sealed in methanol-rinsed brown jars until extraction.

2.3. Extraction and analysis

The extraction and clean-up methods were described elsewhere and were used with minor modifications (Higgins et al., 2005). Briefly, the sediments (1–8 g) were weighed into 50 mL methanol-rinsed polypropylene (PP) tubes. Mass labelled internal standards (400 pg) (Table S2) were spiked into the sediments, and then 10 mL methanol was added. The sediments were soaked and rotated for 30 min. After

Table 1
Global comparison of PFOA and PFOS concentrations in surface sediment (ng/g dw).

Location	Sampling year	n	PFOS	PFOA	Reference
China					
Haihe River	2010	16	1.8–7.3	0.9–3.7	Li et al., (2011a)
Dagu Drainage River	2010	8	0.09–2.3	0.27–1.7	Li et al. (2011a)
Yangtze River estuary	2008	4	72.9–536.7	na	Pan and You (2010)
Yangtze River near Shanghai	2009	9	nd–0.46	0.20–0.64	Bao et al. (2010b)
Zhujiang River	2009	13	nd–3.1	0.09–0.29	Bao et al. (2010b)
Hun River	2008	4	0.13–0.37	0.08–0.17	Bao et al. (2009)
Xi River	2009	7	nd	0.18–48	Bao et al. (2010a)
Liao River	2009	14	0.04–0.48	0.02–0.18	Yang et al. (2011)
Taihu Lake	2009	18	0.06–0.31	0.02–0.52	Yang et al. (2011)
North Bohai Sea coast	2008	35	nd–1.97	nd–0.542	Wang et al. (2011)
Baiyangdian Lake	2008	18	0.11–0.64	<0.1–0.3	Shi et al. (2012)
Laizhou Bay	2009	26	<0.03–0.06	0.07–1.8	This study
Laizhou Bay adjacent rivers	2009	24	<0.03–1.6	<0.04–76.9	This study
Other area around the world					
Tokyo Bay, Japan	2004	1	1.66	0.45	Zushi et al. (2010)
Ariake Sea, Japan	2004	5	0.09–0.14	0.84–1.1	Nakata et al. (2006)
Savannah River estuary, USA	2007	5	0.3–0.8	nd–0.2	Senthil et al. (2009)
LCP Superfund Site, USA	2006	10	0.1–0.4	nd–0.2	Senthil et al. (2009)
Willamette River, USA	2006	4	nd	0.18	Higgins et al. (2007)
San Francisco coast, USA	2002, 2004	13	nd–3.07	nd–0.625	Higgins et al. (2005)
Sydney Harbour, Australia	2009	5	0.80–6.2	0.2–0.16	Thompson et al. (2011)
Orge River, France	2010	3	4.3 ± 0.3	<0.07	Labadie and Chevreuil (2011)
Roter Main River, Germany	2006	11	0.07–0.31	0.02–0.07	Becker et al. (2008)

nd: not detected; na: not available.

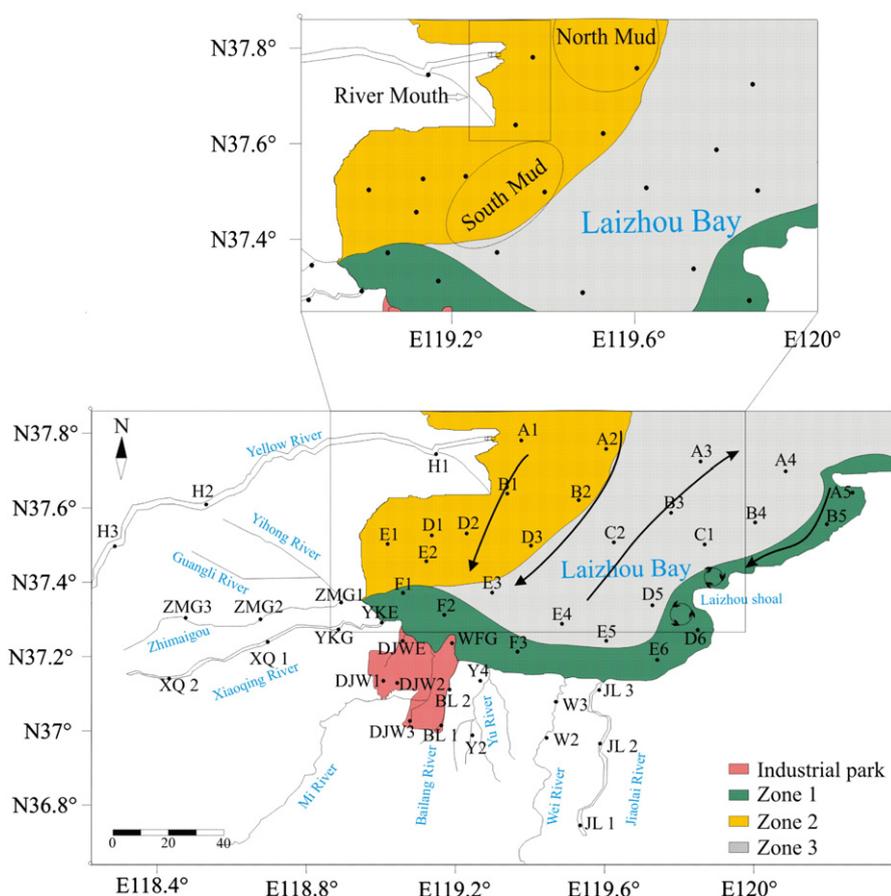


Fig. 1. Sampling locations of Laizhou Bay and adjacent rivers. Zone 1: the area is mainly influenced by the terrestrial source; Zone 2: the area is mainly influenced by the Yellow River input; Zone 3: the area is influenced mainly by marine source or both marine and terrestrial sources (Chen et al., 2006; Hu et al., 2011; Yang et al., 1989). The solid lines with arrows indicate the marine currents directions in Laizhou Bay (Qiao et al., 2010). The circles with arrows indicate the current circulations near the Laizhou Shoal (Wang et al., 2009).

being sonicated for 30 min, the samples were centrifuged for 8 min at a speed of 3000 rpm. The supernatant was transferred to a glass flask for further treatment. The sonication was repeated twice, and finally, 30 mL of the supernatant was pooled. The pooled supernatant was concentrated to ~3 mL, using a rotary evaporator and then loaded onto pre-cleaned ENVI-Carb tubes (3 mL, 0.25 g). Ten millilitres of 0.1% NH_4OH in methanol was added to the cartridges to wash the analytes. The sample volume was reduced to 150 μL using nitrogen evaporators, and 50 μL (20 $\text{pg}/\mu\text{L}$ in methanol) mass labelled 8:2 fluorotelomer unsaturated acids (8:2 FTUCA) was spiked into the vials as an injection standard before instrumental measurements were performed.

The instrumental analysis was performed using a high performance liquid chromatography–negative electrospray ionisation–tandem mass spectrometry system (HPLC–(–)ESI-MS/MS) that consisted of an HP 1100 HPLC system (Agilent Technologies) coupled to an API 3000 triple–quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX). The Teflon parts of the HPLC system were replaced with PP parts to avoid contamination. The mobile phases were Millipore water [A] and methanol [B], which both contained 10 mmol/L ammonium acetate. The chromatographic gradient started with 30% [B] and then increased to 70% [B] over 3 min. After continuously increasing to 100% [B] over 28 min, the gradient was held for 7 min at 100% [B]. The acquisition time was 40 min with 7 min of equilibration. The API 3000 mass spectrometer was operated in multiple reaction monitoring (MRM) mode. The precursor and product ions are listed in Table S1. More details of the instrument analyses can be found elsewhere (Ahrens et al., 2009a). The total organic carbon (TOC) was determined

by an elemental analyser (LECO RC 612). The D50 median diameter sediments were determined by a laser grain size analyser (Malvern Mastersizer 2000F). The statistical analysis was performed using SPSS 16.0.

2.4. Quality assurance and quality control

One blank sample with sodium sulphate as the matrix and one duplicate sample were prepared for each extraction batch (10 samples). The results of the duplicated samples showed a deviation within $\pm 25\%$. Five substances were detected in blank samples: i.e. PFPA (mean 3.3 pg/g dw), PFHxA (mean 17 pg/g dw), PFHpA (mean 60 pg/g dw), PFOA (mean 8 pg/g dw) and PFOS (mean 14 pg/g dw). The instrumental detection limit (IDL) was determined using a signal-to-noise ratio of 3, and the method detection limit (MDL) was defined using a signal-to-noise ratio of 10 for the analytes, which were not detected in the blank samples. For PFPA, PFHxA, PFHpA, PFOA and PFOS, the MDL was extrapolated under 98% confidence intervals using the standard deviations and concentrations in the blank samples. Three sediment samples (4.35 g, 4.61 g and 5.08 g) collected from the Arctic Ocean were tested, and no PFAAs were detectable. The mixture of the PFAA-free samples was used for the matrix spike test. The recoveries of matrix spike samples varied from 52% (PFBA) to 125% (PFUnDA), with an average value of $87\% \pm 16\%$. The recoveries in riverine and coastal samples from Laizhou Bay ranged from $61\% \pm 17\%$ ($^{18}\text{O}_2\text{PFHxS}$) to $88\% \pm 23\%$ ($^{13}\text{C}\text{PFUnDA}$), and the results were recovery corrected.

3. Results and discussion

3.1. Spatial distribution and profiles of PFAAs in surface sediments

Fourteen PFAAs were detected in the surface riverine sediments, namely, C₅-, C₆-, and C₈–C₁₄-PFCAs, and C₄-, C₆–C₈-, and C₁₀-PFSAs. Table 2 summarises the concentrations of PFAAs in the riverine and coastal sediments (Table S3 shows the data in detail). Figs. 2, 3, and 4 show the spatial distributions of PFOA, PFCAs without PFOA, and PFSAs in the Laizhou Bay and nearby riverine sites. The \sum PFAA concentrations ranged from 0.01 ng/g dw to 87.5 ng/g dw (mean: 5.25 ng/g dw; median: 0.72 ng/g dw) in the riverine sediments. The highest concentration (87.5 ng/g dw) of \sum PFAAs was detected in the Xiaoqing River (XQ2). This value was more than one order of magnitude higher than the average value (5.25 ng/g dw) and eight times higher than the second highest value (11.8 ng/g dw), which was detected near the estuary of the same river (YKG). The Xiaoqing River, a man-made river with a total length of 240 km, receives urban, industrial, and agricultural wastewater and sludge and discharges into the Laizhou Bay. The high concentrations might be a result of transportation from the upper stream as well as local release. The spatial distribution of PFAAs was also influenced by human activities. For instance, a flood gate at the upstream XQ1 site interferes with the sediment transport to the Laizhou Bay. As a result, the \sum PFAA concentration at XQ1 (2.91 ng/g dw) was two times lower than the concentration at XQ2. The sediment stopped by the flood gate can be removed to the landfill or used to reclaim farmlands or burn bricks, which act as a secondary PFAA source for soils (Busch et al., 2010; Chaney et al., 1996). Sediments from the Mi River and its tributaries in the industrial park (DJW1, DJW2, DJW3, and DJWE) also exhibited relatively high levels of \sum PFAAs (0.67 ng/g dw to 6.67 ng/g dw). Since the 1990s, the government in this region has strongly fostered the coastal chemical industry, i.e., salt and other chemicals, petro-chemicals, pesticide manufacturing and fluorine-containing chemicals, due to the abundant underground brine resources. Due to the prosperous industrial activities, a large volume of organic pollutants might have been unintentionally produced and discharged without proper treatment. The concentrations of PFAAs in the Yellow River were near the MDL. In 2009, scouring, instead of siltation, occurred in the downstream part of the Yellow River. Thus, the surface sediment collected was decades old from a time when PFAAs were not widely used (Wang et al., 2010). Moreover, the

sorption of PFAAs on organic matter had been confirmed to be more important than the sorption on mineral surface by Higgins and Luthy (2006). The TOC content in the Yellow River sediments ranged from 0.04 to 0.08%, indicating a weak affinity for PFAAs. Excluding the samples in the Xiaoqing River, the PFAA levels in other riverine sediments varied from 0.01 ng/g dw to 1.94 ng/g dw (mean: 1.02 ng/g dw).

PFOA and PFOS were detected in 40% and 42% of the river samples, respectively. PFOA concentrations ranged from 0.04 ng/g dw to 76.2 ng/g dw (mean: 5.19 ng/g dw; median: 0.55 ng/g dw) and accounted for 2% to 93% of the \sum PFAA concentrations. Meanwhile, the PFOS levels were much lower (0.02 ng/g dw to 1.62 ng/g dw; mean: 0.21 ng/g dw, median: 0.04 ng/g dw) and accounted for 1% to 77% of the \sum PFAA concentrations. C₉–C₁₄-PFCAs were detected in 8% to 40% of the samples, and the contributions were between 3% and 43% (mean: 13%) to \sum PFAA concentrations. PFBS and PFHxA had been widely detected in the water and sediment of urban rivers (Labadie and Chevreuril, 2011; Möller et al., 2010; Wang et al., 2011). In the rivers of Laizhou Bay, the concentrations of PFBS in sediments were near the MDL, whereas those of PFHxA were below the MDL at most sampling sites except for the heavily contaminated sites, namely, XQ1 and YKG. Except for the Yellow River and the Xiaoqing River, PFOA was the predominant compound at all estuary sites with a contribution of 69%–93%, while the compositions in the upper stream samples were much different. PFHxS was the dominant compound in the upstream portion of the Mi River (68% at DJW3), the Zimaigou River (61% at ZMG2 and 26% at ZMG3) and the Wei River (56% at W2), and PFOS contributed 77% to the total concentration (Y2) in the Yu River and 42% (JL1) to 53% (JL2) in the Jiaolai River. The difference of congener profiles in rivers might attribute to the different land use patterns and the nearby sources.

Eleven PFAAs were quantified in the coastal sediment, namely, C₅-, C₈–C₁₁-, and C₁₃-PFCAs, and C₄-, C₆–C₈-, and C₁₀-PFSAs. \sum PFAA concentrations varied from 0.12 ng/g dw to 2.1 ng/g dw (mean: 0.76 ng/g dw; median: 0.58 ng/g dw), which were much lower than the concentration observed in the river sediment (0.01 ng/g dw to 87.5 ng/g dw, mean: 5.25 ng/g dw and median: 0.72 ng/g dw). PFOA concentrations were higher than the PFSA concentrations in 88% of the coastal samples. The highest concentration of \sum PFAA was found in the middle of the bay (site D3). PFOA was the predominant contaminant in all samples and accounted for 17% to 97% of the total concentrations. PFOA concentrations varied from 0.07 ng/g dw to 1.81 ng/g dw (mean: 0.54 ng/g dw; median: 0.43 ng/g dw). The highest PFOA concentration was also detected at site D3. PFOS concentrations varied from <MDL to 0.06 ng/g dw (mean: 0.04 ng/g dw; median: 0.04 ng/g dw). Higher concentrations of other PFCAs (other than PFOA) were detected in the inner bay rather than at the coast (Fig. 3). The southern coast in Zone 1 showed significantly lower concentrations of PFSAs than other coastal areas (Fig. 4).

3.2. Global comparison of PFAAs in sediments

Compared with other river and coastal sediments worldwide, the sediment from the Xiaoqing River and the rivers near the industrial park in this study exhibited the highest concentrations of PFOA (2.6 ng/g to 76.9 ng/g) (Table 1). Except for the extremely high-level PFOA sites, PFOA levels at other sampling sites (<MDL to 1.81 ng/g dw) were lower than those of the Haihe River (0.9 ng/g to 7.3 ng/g dw) and Dagou Drainage River (0.27 ng/g to 1.7 ng/g dw) (Li et al., 2011a) and were quite comparable with the concentrations observed in the river and coast sediments from other locations in China (0.08 ng/g to 1.7 ng/g dw in Hun River, 0.20 ng/g to 0.64 ng/g dw in Yangtze River and 0.09 ng/g to 0.29 ng/g dw in Zhujiang River) (Bao et al., 2009, 2010b), Japan (0.45 ng/g to 1.1 ng/g dw) (Nakata et al., 2006; Zushi et al., 2010) and the USA (nd to 0.625 ng/g dw) (Senthil et al., 2009). PFOS levels in sediments from the Laizhou Bay and adjacent rivers in this study (0.02 ng/g to

Table 2
Summary of PFAA concentrations in the Laizhou Bay (unit: ng/g dw).

	Riverine sediment				Coastal sediment			
	Max	Min	Mean	Median	Max	Min	Mean	Median
Ø (D50,µm)	251.7	16.9	68.8	54.2	77.4	8.4	40.3	42.2
TOC (%)	8.96	0.05	0.87	0.39	0.66	0.05	0.29	0.24
PFBS	0.60	0.02	0.12	0.04	0.04	0.02	0.03	0.04
PFHxS	0.52	0.04	0.20	0.16	0.32	0.02	0.09	0.07
PFHpS	0.91	0.10	0.37	0.11	0.17	0.09	0.13	0.13
PFOS	1.6	0.02	0.21	0.04	0.06	0.03	0.04	0.04
PFDS	0.07	0.07	0.07	0.07	0.12	0.09	0.10	0.09
PFPa	2.5	0.00	0.14	0.01	0.02	0.01	0.01	0.01
PFHxA	1.9	0.03	0.43	0.12	–	–	–	–
PFOA	76.9	0.04	5.19	0.55	1.8	0.07	0.54	0.43
PFNA	0.64	0.01	0.08	0.02	0.08	0.01	0.03	0.02
PFDA	1.21	0.01	0.09	0.02	0.06	0.01	0.02	0.02
PFUnDA	0.86	0.01	0.09	0.03	0.07	0.01	0.03	0.03
PFDODA	0.81	0.01	0.11	0.02	–	–	–	–
PFTriDA	0.41	0.01	0.05	0.02	0.03	0.01	0.02	0.02
PFTeDA	0.26	0.01	0.08	0.03	–	–	–	–
\sum PFCAs	86	0.01	4.8	0.30	2.0	0.12	0.64	0.50
\sum PFSAs	1.9	–	0.40	0.18	0.41	0.00	0.12	0.09
\sum PFAAs	87	0.01	5.2	0.72	2.1	0.12	0.76	0.58

–: not available.

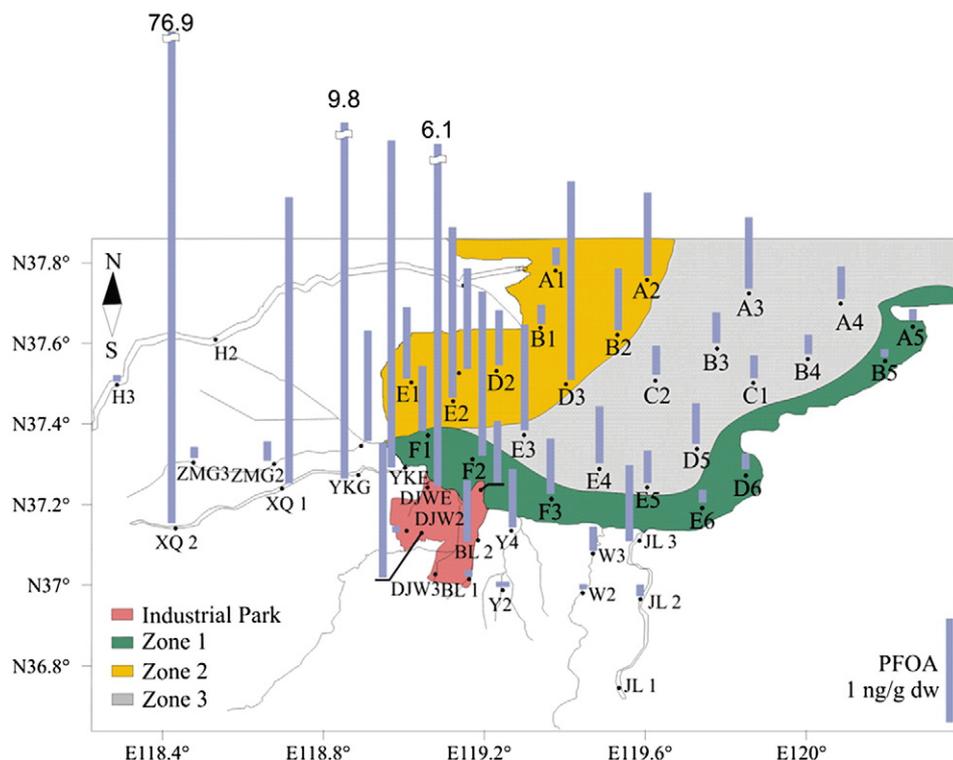


Fig. 2. Distribution of PFOA in coastal and river sediments from Laizhou Bay and its adjacent area.

1.6 ng/g) were lower than the levels reported in some urban rivers in China, namely, the Haihe River (1.8 ng/g to 7.3 ng/g dw), the Dagu Drainage River (0.09 ng/g to 2.3 ng/g dw) (Li et al., 2011a) and the Zhujiang River (ng to 3.1 ng/g dw) (Bao et al., 2010b), but were higher than the levels reported in Taihu Lake (0.06 ng/g to 0.31 ng/g dw) (Yang et al., 2011) (Table 1). Wang et al. (2011) investigated the PFOS

concentrations on the northern coast of the Bohai Sea, which were higher (up to 1.97 ng/g dw) than the concentrations presented in this study. Compared with previous studies from other countries, the concentrations of PFOS in this study, with mean values of 0.21 ng/g dw in river sediments (extremely high concentrations in the Xiaoqing River sediment were excluded) and 0.04 ng/g dw in coastal sediments, were lower

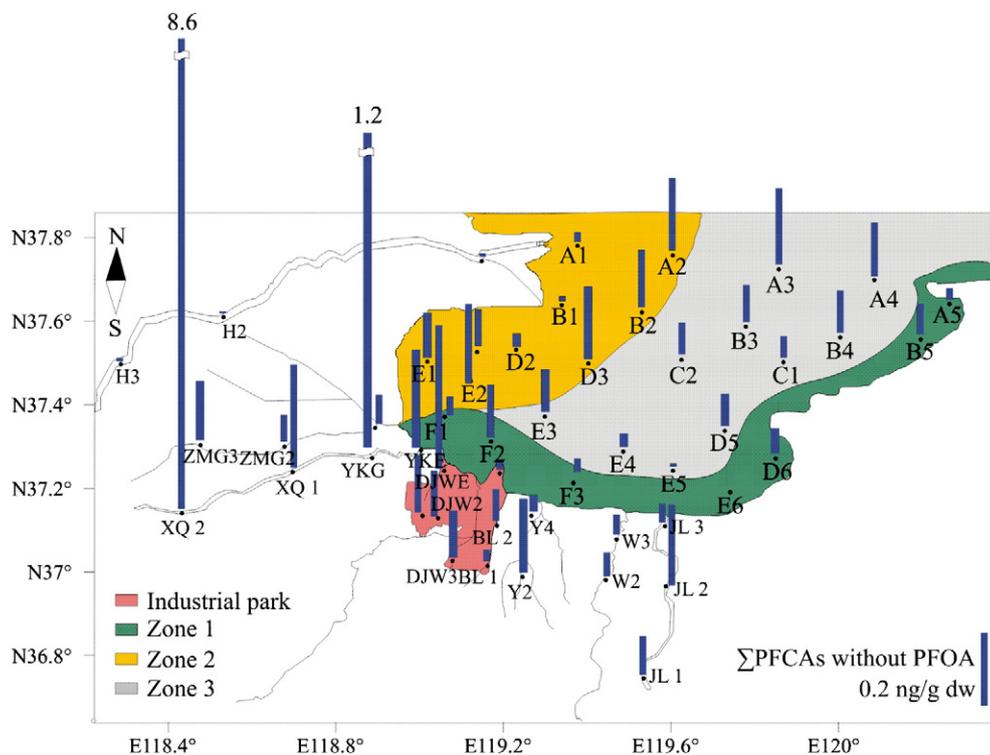


Fig. 3. Distributions of Σ PFCAs without PFOA in coastal and river surface sediment in Laizhou Bay and its vicinity.

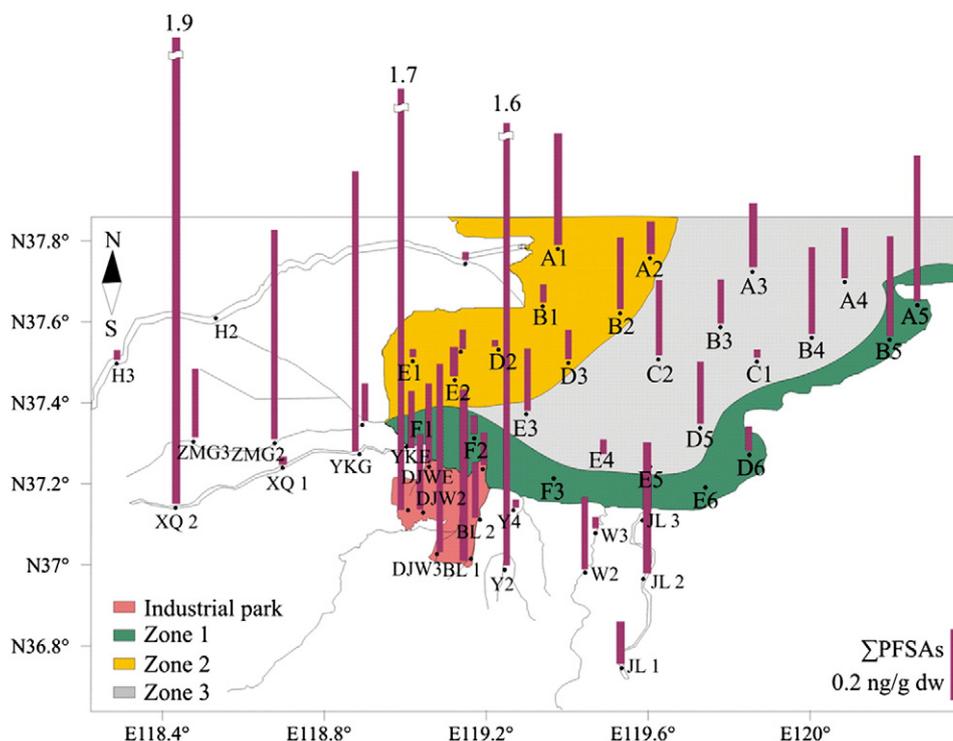


Fig. 4. Distributions of Σ PFSAs in coastal and river surface sediment in Laizhou Bay and its vicinity.

than those observed in the Orge River, France (4.3 ± 0.3 ng/g dw) (Labadie and Chevreuil, 2011), Sydney Harbour, Australia (0.80 ng/g to 6.2 ng/g dw) (Thompson et al., 2011) and the San Francisco coast, USA (nd to 3.07 ng/g dw) (Higgins et al., 2005). However, the concentrations of PFOS in this study were quite comparable with the concentrations reported in the Savannah River estuary, USA (0.3 ng/g to 0.8 ng/g dw) (Senthil et al., 2009), Roter Main River, Germany (0.07 ng/g to 0.31 ng/g dw) (Becker et al., 2008) and the Ariake Sea, Japan (0.09 ng/g to 0.14 ng/g dw) (Nakata et al., 2006).

The concentrations of PFOS were generally higher than the concentrations of PFOA in sediments (Table 1) due to the stronger affinity of PFOS than PFOA in sediments (Ahrens et al., 2011; Higgins and Luthy, 2006), but exceptions were also reported. Yang et al. (2011) reported slightly higher concentrations of PFOA than PFOS in the sediments from the Taihu Lake, and a similar composition pattern was also observed in the dissolved phase. Nakata et al. (2006) detected significantly higher concentrations of PFOA than PFOS in the Ariake Sea, Japan, and considered different partitioning behaviours to be the main cause. PFOA concentrations in the coastal sediment of the Laizhou Bay were all higher than PFOS concentrations. On the basis of this composition pattern, higher concentrations of PFOA than PFOS were expected in the dissolved phase. The same profile pattern was observed in the sediments of the Xiaoqing River and the rivers near the industrial park (Table S3). The PFOA concentration at sampling site XQ2 was 70-fold higher than the PFOS concentration, whereas the PFOA level at D3 was 60-fold higher than the PFOS level. To the best of our knowledge, only Bao et al. (2010a) have reported significantly higher concentrations of PFOA than PFOS in river sediments from the Xi River, which is located near a fluorochemical plant. The manufacture of polytetrafluoroethylene (PTFE) was considered to be the source of PFOA. The highly elevated levels of PFOA in the Xiaoqing River could be attributed to the production of PTFE, petrochemical industry and other chemical industries along this river. Several chemical plants are located within the industrial park, and the usage and/or manufacture of PFOA-containing products could be the source of PFOA. To our knowledge, the total amount of PFOA manufactured and used in China had not been reported officially. Mei (2008) investigated the manufacture

of PFOA-containing products and estimated the demand for PFOA in China to be 100 t/a. The production and/or use of PFOA in the industrial park were unknown quantities at the time of this analysis, and it was difficult to estimate the amount of PFOA released into the environment. However, the detection of PFOA in sediment reminds both scientists and the government that more attention should be paid because of the high levels of this compound. In addition, further study is urgently needed to mitigate the emission of PFAAs and assess the possible health effects of these substances.

3.3. The dynamics of distribution in Laizhou Bay

Higgins and Luthy (2006) demonstrated that the sorption of PFAAs onto the sediment was related to the organic carbon content (TOC) of the sediment. The coastal sediments of the Laizhou Bay showed a positive relationship between TOC and Σ PFAAs ($r^2 = 0.50$, $n = 23$, $p < 0.001$), as well as between TOC and PFOA concentrations ($r^2 = 0.32$, $n = 23$, $p < 0.001$). TOC content in the sediment correlates well with the D50 median diameter ($r^2 = 0.47$, $n = 23$, $p < 0.001$), indicating that fine particles had a stronger affinity for organic matter than coarse particles (Sugui, 1973). Consequently, grain sizes could influence the distribution and partitioning of PFAAs via their impact on the affinities of organic matter for sediments (Hu et al., 2011; Zheng et al., 2011). PFAAs might adsorb onto fine particles because there was more organic matter on/in such particles. Moreover, the fine particles have a larger specific surface area, which could include more adsorption sites. The D50 median diameters were significantly related to the PFAA ($r^2 = 0.30$, $n = 26$) and PFOA ($r^2 = 0.19$, $n = 26$) concentrations at the $p < 0.05$ level, which could support the hypothesis above.

The southern coast (sites F1, F2, and F3 in Zone 1) of the Laizhou Bay is highly influenced by the adjacent land use pattern (Pan et al., 2011a). Σ PFAA concentration levels in the nearby shore sediments were lower than the observed concentrations in the estuaries due to the broader river bed and the dilution effect. The concentration of Σ PFAAs at site F2 (1.7 ng/g dw) was higher than that at site F1 (0.65 ng/L) and F3 (0.55 ng/L), which could be attributed to the riverine discharge, most likely from the Xiaoqing River. The concentration

of Σ PFAAs at site F2 was significantly lower than the concentrations in the Xiaoqing River (YKE, YKG, XQ1, and XQ2), and the main reason for this difference was the dilution effect caused by seawater from the river–estuary–nearshore gradient.

The eastern coast of the Laizhou Bay is affected by several small rivers with lengths of less than 50 km and an average annual runoff of less than 26 million m³ (Li and Zhao, 2002); thus, no sediment samples were collected from these rivers. Except for several small fishing ports, this area does not have intensive industrial activity, and the coastal region was mainly characterised by farm land and salt fields. The PFOA concentrations at A5, B5, D6, and E6 were lower than those at other sites in Zone 1, whereas C₄–C₁₀-PFSAs showed relatively higher levels at A5 and B5. A5 and B5 were located near the Longkou Port where many fishing ships are docked. The occurrence of PFAAs at these two sites can be attributed to the release from fishing activities, for instance, the maintenance of the water-proof fishing tools and ships. The alongshore current transports terrestrial sediment from Qimu Island to Laizhou Shoal along the eastern coast of Laizhou Bay (Fig. 1). The clockwise tidal residual current circle caused by the tide and influenced by the geographic conditions captures sediments and builds up the shoal (Wang et al., 2009). Hence, PFAAs detected at A5 and B5 might be transported to the Laizhou Shoal. The southwest flank of the shoal has been eroded by the tidal current. The anti-clockwise tidal current also creates a deposition centre at the location of the D6 sampling site. D6 receives sediment from the erosion of the shoal and transportation across the headland cape. The ultimate sources are the eastern coast rivers.

Shear fronts, tidal currents, and storm waves control sediment dispersion near the Yellow River delta (Bi et al., 2010). Most of the suspended sediment cannot be transported farther than 30–35 km eastward from the coast (Qiao et al., 2010; Yang et al., 1989). The water depth within this region is less than 15 m (Bi et al., 2010; Yang et al., 1989). The southward transport is limited to approximately 37.35° N by the strong tidal current (Chen et al., 2006). This study included approximately nine sampling sites in the Yellow River-derived sedimentation zone (Zone 2), namely, A1, A2, B1, B2, D1, D2, D3, E1, and E2. Significant relationships between the concentrations of PFOA and TOC ($r^2 = 0.45$, $n = 9$, $p < 0.05$), PFCAs (excluding PFOA) and TOC ($r^2 = 0.87$, $n = 9$, $p < 0.001$), and PFAAs and TOC ($r^2 = 0.56$, $n = 9$, $p < 0.05$) were observed. This finding supports the organic carbon-dependent distribution of pollutants. The concentrations of PFAAs in Zone 2 (mean: 2.1 ng/g dw) were much higher than the concentrations in the Yellow River (0.24 ng/g dw). This phenomenon was partly attributed to the higher TOC content of the Zone 2 sediments (0.14% to 0.63%) compared to the Yellow River sediments (0.05% to 0.08%).

Figs. 2 and 3 show that increasing distribution trends of PFCAs were observed in the river mouth eastward to the Zone 2 boundary. Fig. 4 shows that the PFSAs distribution was similar to that of the distribution of PFCAs, except for a relatively high concentration at site A1. Relatively high concentrations of PFCAs and PFSAs were detected in the southeast region of the Yellow River Delta.

These distribution characteristics may be due to the joint effects of source region of pollutants, hydrological processes, and suspended particle and pollutant interactions in Laizhou Bay. First, in this study, the Xiaoqing River was assumed to be the major source of PFOA in Laizhou Bay, as can be inferred from the notably high levels of PFOA in the sediment samples and the large volume of runoff from the Xiaoqing River (mean of 0.85×10^9 m³/a from 1950 to 1994) compared to other rivers (except the Yellow River, with a mean of 42.3×10^9 m³/a) flowing into Laizhou Bay (Li and Zhao, 2002). Second, the sediment from the Yellow River is deposited in two major regions, one in the northeast part of the bay (North Mud in Fig. 1) and the other to the southeast of the river mouth (South Mud) (Qiao et al., 2010). In September 2009, approximately 2 640 000 t of sediment were discharged from the Yellow River into Laizhou Bay, accounting for 4.7% of the total discharge for

the whole year (Yellow River Conservancy Commission, 2009). Coarse particles were deposited near the river mouth, whereas fine particles were dispersed farther into the inner bay by currents and tides. Third, the suspended particles transported from the Yellow River mouth might encounter the high levels of PFAAs from the Xiaoqing River, undergo sorption/deposition/re-suspension/re-deposition processes and become deposited in the South Mud zone. The re-suspension of surface sediment by tidal current increased the suspended sediment concentration at the two mud regions and weakened the sedimentation process. Additionally, water disturbances mixed the particles and PFAAs sufficiently and provided more opportunities for PFAAs sorption from the dissolved phase onto the particles. The suspended sediments are deposited in these regions when entrapped by the circulations of residual tidal currents in the North and South Mud areas near the river mouth. Higher concentrations of PFOA were detected in this area because of the substantial interaction between the water and the suspended particles, as well as the finer size of the sediments. These factors together resulted in the high levels of PFOA at the D3, which is located in the South Mud zone and east of the Xiaoqing River mouth. For PFAAs other than PFOA, the Yellow River might act as a potential source, considering the huge annual runoff. However, due to the absence of data about PFAAs in the dissolved phase from these rivers, the exact input sources require further investigation.

Except for the coastal area, which is dramatically influenced by the terrestrial input, the sediments in other parts of the Laizhou Bay were affected by both terrestrial and marine sources related to biogenic particles that contained at least 30% of skeletal of marine organisms (Hu et al., 2011; Yang et al., 1989). The main direction of the current in Zone 3 is northeast, which is opposite that of the flow current in the South Mud region and the alongshore current of the east coast of the Laizhou Bay (Fig. 1). This current is one of the major dynamic forces transporting the sediment off the Laizhou Bay; another major force is the anti-clockwise circulation to the northeast of the Yellow River mouth in Zone 2. The PFCAs concentrations were higher at the mouth of the bay than in the inner region. The levels of PFAAs in the sediments of Zone 3 were also significantly correlated with the TOC contents of the sediments ($r^2 = 0.70$, $p < 0.01$, $n = 9$). The PFSAs distribution pattern was complicated, and the concentrations were higher than the concentration observed in the southern coast sediment. Different from other neutral persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethanes (DDTs), the ionic PFAAs were mostly observed in the dissolved phase and were transported by the marine currents. PFAAs transported from the source regions via river and currents can be adsorbed onto the biogenous sediments and can elevate their levels in the central bay. Li et al. (2005) demonstrated by modelling that the Lagrangian residual current, which is a periodic and influenced by wind, tide and salinity, was weak in the Laizhou Bay in autumn. This phenomenon indicated the weak transportation of PFAAs off the bay via residual current, and more chances for the pollutant adsorbing onto sediments. PFAAs on the sediment finally moved out of the Bohai Sea to the North Yellow Sea via the marine currents. The distribution dynamics of PFAAs in the surface sediments was a combination of hydrological and geomorphological conditions, as well as the organic carbon content of the sediment. Due to the relatively higher water solubility of PFAAs than other POPs, PFAAs could be transported farther by currents and adsorb onto the sediment in the open area. Hence, the distribution patterns of PFAAs were different from those of other neutral POPs, such as OCPs and PBDEs.

3.4. Preliminary environmental risk assessment

The aquatic toxicology of PFAAs had been investigated by previous studies involving drinking water and aquatic organisms (Giesy et al., 2010; Zushi et al., 2012). Lin et al. (2010) assessed the environmental risk of PFOA and PFOS in Nanmen River water and indicated that PFOS

concentrations up to 6.05 µg/L posed great risk to local ecosystem. In this study, the preliminary environmental risk assessment (ERA) based on the risk quotient (RQ) was performed in sediments from Laizhou Bay and its vicinity to investigate the potential risk for the local environment.

The RQ was defined as the ratio of the measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC). The PNEC of the sediment can be derived from a) the no observed effect concentration (NOEC) or the median effect/lethal concentration (E/LC50) with an assessment factor (AF); and b) the equilibrium partitioning method when the toxicity data are unavailable (Lepper, 2002). The PNECs of PFOA and PFOS for benthic animals in Laizhou Bay had been scarcely reported in the literature. In this study, the PNECs of river sediment were derived by the equilibrium partitioning method. The PNECs for fresh water (1250 µg/L for PFOA and 25 µg/L for PFOS) were cited from Colombo et al. (2008) and Brooke et al. (2004), and the organic carbon normalised partitioning coefficient ($\log K_{oc}$ (L/kg_{oc}), 2.11 for PFOA and 2.68 for PFOS) came from Higgins and Luthy (2006). PNECs vary depending on the matrices. The values for the coastal sediment were 10 times lower than the value observed in the fresh water. Both the PNECs and the real sample concentrations were TOC-normalised. As presented in Table S5, the highest TOC-normalised concentration of PFOA was 15 ng/g/TOC% dw at site DJWE, followed by 8.6 ng/g/TOC% dw at site XQ2. As presented in Table S6, the RQs of PFOS and PFOA were all below 1, indicating that no significant risks were detected in the river and coastal sediments. The highest PFOS and PFOA concentrations (0.24 ng/g/TOC% dw for PFOS and 5.5 ng/g/TOC% dw for PFOA) in coastal sediments were closer to the threshold (RQ: 0.122 for PFOS and RQ: 0.209 for PFOA) than river samples. The non-TOC-normalised PNECs were also determined to compare the results using a different method. The K_d values for fresh water sediment were 0.1973 L/kg for PFOS and 0.0690 L/kg for PFOA (Ferrey and Wilson, 2009). To the best of our knowledge, these K_d values were the lowest ones observed, indicating that the PNECs were overestimated. The RQs were still all below 1 (Table S6), while the highest concentration of PFOA (76.9 ng/g dw) at XQ2 was quite close to the PNEC threshold (86 ng/g dw), suggesting a potential threat to the aquatic ecosystem.

A considerable uncertainty had been associated with the PNEC values derived via the partitioning method. The partitioning coefficient may differ between marine and fresh water systems, and the factor of 10 may not be suitable for Laizhou Bay. If organic matter was introduced to PNECs, the conclusion might be different from the one for which organic matter was not considered. The organic matter in the sediment might enhance the intake of PFAAs; thus the PNEC values for the sediment should be revised.

In previous studies, Pan et al. (2011a, 2011b) and Zhong et al. (2011) used the same set of sediments to investigate the levels and distributions of OCPs, PBDEs and polychlorinated naphthalenes (PCNs) in Laizhou Bay and adjacent rivers. Relatively high concentrations of these POPs were found in the industrial park (Pan et al., 2011a, 2011b; Zhong et al., 2011). The sediments in the Xiaoqing River exhibited high concentrations of DDTs and BDE209 but not hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) and other PBDEs excluding BDE209. OCPs, PBDEs, and PFAAs showed relatively high concentrations in the coastal sediment from the inner bay but not in the coastal area, whereas PCNs did not show an obvious distribution trend.

For OCPs and PBDEs, the ERAs were also performed to determine the most threatening substances (Table S7). For PBDEs, the assessment method was similar to that used for PFOA and PFOS (Table S6), and no significant risks were predicted in coastal and river sediments. For OCPs, a five-level classification for a Norwegian aquatic ecosystem, which was based on PNEC, was suggested as the coastal sediment quality criteria for Laizhou Bay and vicinity (Bakke et al., 2010). Under these criteria, Class I represents the background range; Classes II and III are the PNECs for chronic and acute exposure respectively; Class IV is 2–5 times the PNEC values, depending on the substances; and Class V

includes the levels that are above class IV. HCB concentrations in the coastal sediment were Class I, which represents the background level. Lindane and \sum DDTs in the river and coastal sediments and HCB in the river sediment belong to Class II, based on the PNEC for chronic exposure. Class II indicates adverse effects from long-term exposure. The levels in this study were all near the low end of the reference ranges, suggesting mild-to-moderate threats. The ERA of PCNs was not determined due to the lack of data.

The ERAs for DDTs, lindane, HCB, pentaBDE, decaBDE, PFOS, and PFOA in the Laizhou Bay and adjacent rivers were negligible (Tables S6 and S7). At sampling site XQ2, the river sediment, which had a PFOA concentration of 76.9 ng/g dw, was close to the PNEC threshold (86 ng/g dw) and might pose a potential threat to the aquatic ecosystem.

4. Conclusions

High concentrations of PFAAs in the Xiaoqing River and industrial park were attributed to the urbanisation and industrial development. PFOA was the predominant compound, and the highest concentration detected in Xiaoqing River sediment (76.2 ng/g dw) was higher than any other concentrations reported worldwide. Due to their hydrophilic characteristics, the distributions of PFAAs in the coastal sediments were strongly influenced by hydrological dynamics. The preliminary environmental risk assessment proved negligible for PFOA and PFOS as well as OCPs and PBDEs. To minimise the uncertainty of risk assessment in sediment, further studies should be conducted.

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Appendix A. Supplementary data

Supplemental information is available covering details on the target analytes, compound concentrations, global comparison and environmental risk assessment. Supplementary data related to this article can be found online at doi: <http://dx.doi.org/10.1016/j.scitotenv.2012.12.095>.

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