Baseline

Perfluorinated compounds in estuarine and coastal areas of north Bohai Sea, China

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ABSTRACT

Perfluorinated compounds (PFCs) in water, sediment, soil, and biota collected from estuarine and coastal areas of the north Bohai Sea, China, were determined by use of HPLC-MS/MS. Significant concentrations of PFCs were found in water (mean: 18.4 ng/l) and biologic samples (fish: 265 ng/g dw), while concentrations of PFCs in soils and sediments were less. The predominately detected compound was perfluorooctanesulfonate (PFOS), with a maximum concentration of 30.9 ng/l in water and 791 ng/g dw in fish. Concentrations of PFCs were significantly greater in the Liaohe River system than other locations, which suggests point sources in this urbanized and industrialized region. PFOS concentrations in water and biota were both less than the reported threshold concentrations. Detection of PFCs at relatively great concentrations in various environmental matrices from this region suggested that further studies characterizing concentrations of PFCs, their sources and potential risk to both humans and wildlife are needed.

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Perfluorinated compounds (PFCs) have been manufactured since the 1950s, for their unique properties such as high surface activity, thermal and acid resistance, and water and oil repellency (Giesy and Kannan, 2001, 2002). PFCs have been used in a variety of applications such as surfactants and surface protectors in carpets, leather, paper, food containers, fabric, and upholstery and as performance chemicals in products such as fire-fighting foams, floor polishes, and shampoos (Kissa, 2001). Widespread application followed by environmental persistence and bioaccumulation of terminal degradation products of PFCs has resulted in the global occurrence of these substances in air (Barber et al., 2007; Dreyer and Ebinghaus, 2009; Kim and Kannan, 2007), aquatic systems (Fujii et al., 2007; Rayne and Forest, 2009), as well as wildlife species inhabiting not only locations in close proximity to pollution sources, but also in remote areas (Houde et al., 2006; Fatihah et al., 2009).

Among the PFCs, perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) are regarded as the terminal degradation products, and are the chemicals that are most frequently detected in the environmental and biologic samples, and often occur at the greatest concentrations. PFOS was recently listed as a “persistent organic pollutant”, under the Stockholm Convention, but many exemptions were made which allow for continued production and use of some PFCs, especially in China (Wang et al., 2009). In

addition, there are a number of other PFCs used commercially that can occur in the environment, including perfluorooctanesulfonamide (PFOSA), perfluorohexanesulfonate (PFHxS), perfluorobutanesulfonate (PFBS), and perfluorononanoic acid (PFNA) (Giesy and Kannan, 2002; Giesy et al., 2010).

Rapid industrial development in China during the past few decades has transformed China into one of the world's largest economies, especially in the Bohai Sea region; a semi enclosed coastal water body on the northeast coast of China. The Bohai Sea, with its nearby coastal areas and rivers/estuaries, is a major commercial artery and has been a region of significant urbanization and industrialization (Liu et al., 2006). Its proximity to Beijing, the capital of China, makes it one of the busiest seaways in the world. The Yellow, Liaohe, Haihe, Luanhe, and Daling Rivers are major freshwater sources discharging directly into the Bohai Sea. Rapid economic development has brought, and continues to bring about increasing amounts of municipal, industrial and agricultural wastes into the water body. The environmental quality in the estuarine and nearby coastal areas has been adversely affected by intense industrial and urban activities, and the Bohai Sea region is currently one of the most polluted areas in China (Hu et al., 2010; Luo et al., 2010; Naile et al., 2010; Wang et al., 2005).

Recently, concentrations of PFCs in water, sediment, and biota in China have been reported (Chen et al., 2009; Ju et al., 2008; Mak et al., 2009; Pan et al., 2010; So et al., 2007; Zhang et al., 2010). However, previous surveys have been limited in their scales

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and matrices, and relatively few studied sources, distribution, and fate among the multiple matrices including: water, sediment, soil, and biota. The present study was one part of a series studies on Bohai Sea and Yellow Sea pollution, conducted as a systematic investigation to trace toxic substances in various environmental media from marine environment and adjacent riverine and estuarine areas of the Yellow Sea including the Bohai Sea of China and the West Sea of Korea. The objectives of the present study were to determine the concentrations, distribution, and fate of PFCs in environmental matrices to identify the sources, and thus provide information for future management and remediation efforts in the Bohai Sea.

This study focused on the coastal and riverine and estuarine areas of northern Bohai Sea, in north-eastern China, including the following eight cities: Tangshan (TS), Qinhuangdao (QH), Huludao (HL), Jinzhou (JZ), Panjin (PJ), Yinkou (YK), Dalian (DL), and Dandong (DD). 36 water, 31 soil, 35 sediment and 42 biologic samples including fishes, crabs, shrimps, clams, frogs, snails and loaches were collected from 16 estuarine and coastal areas along north Bohai Sea during May of 2008 (Fig. 1). Throughout the survey, a global positioning system (GPS) was used to map the position of each sampling site.

One liter of surface water was collected by dipping a clean, methanol rinsed 1 L polypropylene (PP) bottle just under the surface of the water. Residual chlorine in each water sample was reduced by adding 200 μ l of 200 mg/ml of a sodium thiosulfate solution using a disposable PP syringe. Surface (top 1–10 cm) soil and sediment samples were collected using a clean methanol rinsed stainless steel trowel. Representative samples were prepared by mixing five sub-samples from the area of about 5 m². Samples were transferred and stored in clean PP bags. Biologic samples were collected by hand in coastal tidal pools and along the shores of inland water bodies, and were transferred and stored in clean PP bags. Sample duplicates and field blanks were collected daily, and were analyzed along with laboratory and procedural blanks. All samples were stored on ice for transport to the laboratory and frozen at -20°C until analyses.

Water samples were extracted using Oasis HLB solid phase extraction cartridges (SPE) (0.2 g, 6 cm³) (Waters Corp., Milford, MA) as previously reported (Naile et al., 2010; So et al., 2004). Cartridges were preconditioned by eluting with 10 ml of 100% methanol followed by 10 ml of nano-pure water at a rate of 2 drops a second. 500 ml of water was spiked with 500 μ l of 5 ng/ml of the internal standard (isotopically labeled PFOS and PFOA, PFOS [¹⁸O₂] and PFOA [1,2,3,4-¹³C]) and then loaded onto the cartridge, at a rate of 1 drop a second. Cartridges were then washed with 5 ml of 40% methanol in water and allowed to run dry. Eluents were discarded. Target compounds were eluted with 10 ml of methanol at a rate of 1 drop a second and collected in a 15 ml PP centrifuge tube. The eluate was then reduced to 1 ml under a gentle stream of nitrogen gas, and filtered using a disposable PP syringe, fitted with a disposable nylon membrane Millex filter unit (pore diameter 0.2 μ m, Whatman, Maidstone, United Kingdom). Samples were stored and analyzed in PP auto-sampler vials fitted with PP septa (Canadian Life Science, Peterborough, ON, Canada).

Soil and sediment samples were extracted using a method similar to that described by Higgins et al. (2005) with some modifications. In brief, soils and sediments were freeze-dried and then homogenized with a mortar and pestle and passed through a 2.0 mm sieve to remove pebbles and debris. Approximately 1.0 g samples were transferred to a clean 50 ml PP centrifuge tube, and spiked with 500 μ l of a 5 ng/ml internal standard, to which 10 ml of a 1% acetic acid solution was added. Each tube was then vortexed, and placed in a heated sonication bath for 15 min at 60 $^{\circ}\text{C}$. After sonication the tubes were centrifuged at 3000 rpm for 3 min and the acetic acid solution was decanted into a new clean 50 ml PP tube. An aliquant of 2.5 ml of a 90:10 (v/v) methanol and 1% acetic acid mixture was then added to the original vial and the vial was again vortex mixed and sonicated for 15 min, before being centrifuged and decanted into the second tube. This process was repeated once more, and a final 10 ml acetic acid wash was performed. All extracts were combined in the second tube before being passed through the SPE cartridge in a similar fashion as described above in the water extraction procedure.

Fig. 1. Sampling locations for soil samples (black cross with numbers), water and related sediment (green dots) along north Bohai Sea, biologic samples were collected as well. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Biologic samples were extracted using an alkaline digestion SPE method (So et al., 2006) with minor changes. Each sample was thawed and filleted (skin-on), and composite samples from each sampling location were made by combining fillets of the same species. Then the muscle tissues were freeze-dried, ground, then wrapped in aluminum foil and stored at -20°C until chemical analysis. Approximately 1 g of homogenized tissue sample (dry powder) was transferred to a 50 ml PP centrifuge tube and spiked with 500 μl of 5 ng/ml internal standard, and 30 ml of 0.01 N KOH/methanol was added to the tube. The mixture was then shaken at 250 rpm for 16 h at room temperature. After digestion 5 ml of the resulting tissue solution was added to a 1 L PP bottle containing 100 ml of nano-pure water and shaken thoroughly. This tissue-water mixture was then extracted using SPE cartridges as previously stated for water extraction procedure.

The internal standard consisted of PFOA [$1,2,3,4\text{-}^{13}\text{C}$] (> 98%, Wellington Laboratories, Guelph, ON, Canada) and PFOS [$^{18}\text{O}_2$] (RTI International, USA). The external standard used for all matrix spikes was a mixture of 12 different PFCs (> 98%, Wellington Laboratories) including PFBS, PFHxS, PFOS, perfluorodecane sulfonate (PFDS), perfluorobutyric acid (PFBA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, PFNA, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), and perfluorododecanoic acid (PFDoA), and each at a concentration of 6.0 ng/ml was used as an external standard. HPLC grade methanol and ammonium acetate were purchased from J.T. Baker (Phillipsburg, NJ, USA). Analytical grade sodium thiosulfate was purchased from EMD Chemicals (Gibbstown, NJ, USA). Nano-pure water was obtained from a Milli-Q Gradient A-10 (Millipore, Bedford, MA, USA).

A HP 1200 high performance liquid chromatography system (HPLC) by Agilent Technologies was used for separation of all target analytes. The HPLC was fitted with a Thermo Scientific Betasil C18 ($100 \times 2.1\text{ mm}$, $5\text{ }\mu\text{m}$ particle size) analytical column, and a suitable guard column was used to prevent instrument background contamination. An aliquant of 2 mM ammonium acetate as an ionization aid and methanol were used as mobile phases. Gradient conditions were used at 300 ml/min flow rate and 10 μl of the sample was injected, starting with 60% A (2 mM ammonium acetate) and 40% B (100% methanol). Initial conditions were held for 2 min and then ramped to 20% A at 18 min, held till 20 min, decreased to 0% A at 21 min, increased to 100% A at 22 min, held until 22.5 min, returned to initial condition at 23 min, and finally held constant until 26 min. The temperature of the column oven was kept constant at 35°C .

Mass spectra were collected using an Applied Biosystems SCIEX 3000 (Foster City, CA) tandem mass spectrometer, fitted with an electrospray ionization source, operated in negative ionization mode. Chromatograms were recorded using a multiple reaction monitoring mode (MRM) with a dwell time of 40 ms. The following instrument parameters were used: desolvation temperature (450°C), desolvation (curtain) gas 6.0 arbitrary units (AU); nebulizer gas flow 5 AU; ion spray voltage -3500 V ; and collision gas 12 AU. The optimal settings for collision energies and declustering potential were determined for each analyte's transitions. Quantification using these transitions was performed using Analyst 1.4.1 software provided by SCIEX (Applied Bioscience, Foster City, CA).

In order to insure the accuracy of the sampling, extraction, and analytical procedures, field blanks were obtained with each set of water samples analyzed. Procedural blanks and recoveries were determined for each set of extractions. Quantification was performed using the internal standard method based on $^{18}\text{O}_2$ -PFOS and $^{13}\text{C}_4$ -PFOA as the surrogate. To reduce instrument background contamination coming from the HPLC or solvents, a ZORBEX (Thermo Scientific, $50 \times 2.1\text{ mm}$, $5\text{ }\mu\text{m}$ particle size) column was inserted directly before the injection-valve, as adapted from Benskin et al. (2007). All field and laboratory blanks were below the limit of quantification (LOQ), where the LOQ was defined as 5 times the background noise. The use of Teflon coated lab-ware was avoided during all steps of sample preparation and analysis to minimize contamination of the samples. The ions monitored, method detection limit (MDL), and matrix spike recoveries for all of the chemicals of interest are summarized (Table 1).

Detectable concentrations of waterborne PFCs, were observed at most locations in estuarine and coastal areas of north Bohai Sea (Fig. 2, Table 2). All of the PFCs, except for PFBS, PFHxS, PFDS and PFDoA, were detected in water samples and particularly PFOS, PFOA, PFBA, PFHxA, and PFHpA were detected in more than half of water samples analyzed. Among 12 different compounds were investigated, PFOS and PFOA were consistently found at the greatest concentrations (Fig. 2), except for limited locations in Dalian area (DL locations). Thus the discussion will concentrate on PFOS and PFOA. Almost all of the water samples contained detectable concentrations of PFOS and PFOA. Concentrations of PFOS and PFOA ranged from < LOQ to 30.9 ng/l with a mean of 6.98 ng/l and from < LOQ to 81.7 ng/l with a mean of 14.1 ng/l, respectively. They were found to be the predominant waterborne PFCs accounting for about 62% relative to total.

Table 1

QA/QC of 12 target perfluorinated compounds (PFCs) including limit of quantification (LOQ), method detection limit (MDL) and matrix spike recovery (MSR) for water, sediment, soil, and biologic samples.

Compounds	Acronym	LOQ			MDL			MSR		
		W ^a (ng/l)	S ^b (ng/g dw)	B ^c	W (ng/l)	S (ng/g dw)	B	W (%)	S	B
Perfluorobutanesulfonate	PFBS	0.5	1	1	1	1	1	94	32	97
Perfluorohexanesulfonate	PFHxS	0.1	0.5	1	0.2	0.5	1	136	134	113
Perfluorooctanesulfonate	PFOS	0.1	0.5	0.1	0.2	0.5	0.1	101	95	85
Perfluorodecanesulfonate	PFDS	0.1	0.5	0.1	0.2	0.5	0.1	101	43	68
Perfluorobutanoic acid	PFBA	1	1	1	2	1	1	120	IS ^d	10
Perfluorohexanoic acid	PFHxA	0.5	0.1	0.1	1	0.1	1	85	79	73
Perfluoroheptanoic acid	PFHpA	0.5	0.1	0.1	1	0.1	0.1	103	123	104
Perfluorooctanoic acid	PFOA	0.5	0.5	0.5	1	0.5	0.5	88	89	85
Perfluorononanoic acid	PFNA	1	1	1	2	1	1	132	135	123
Perfluorodecanoic acid	PFDA	0.1	0.1	0.1	0.2	0.1	0.1	93	106	71
Perfluoroundecanoic acid	PFUnA	1	0.5	1	2	0.5	1	112	53	86
Perfluorododecanoic acid	PFDoA	1	0.1	1	2	0.1	0.5	77	70	47

^a W, abbreviation of water.

^b S, abbreviation of soil and sediment.

^c B, abbreviation of biologic samples.

^d IS, Insufficient recovery.

The greatest concentrations of PFCs (121 ng/l) were found at locations JZ5, JZ3 and JZ4 (Fig. 2). These locations contained greater concentrations of all detectable PFCs, except for PFOS. PFOA was the dominant contributor to PFCs in this area, and its concentration in JZ3, JZ4 and JZ5 were 68.1 ng/l, 72.2 ng/l, and 81.7 ng/l, respectively. These samples were collected from the Daling River adjacent to the cities of Jinzhou and Huludao, which has been one of the largest chemical industrial areas of China since the 1960s. There are still oil refining plants, chemical plants, and smelting plants in this region. The Daling River is one tributary of the Liaohe River system, which is one of the most contaminated water bodies in China (Zhang et al., 2006). The greatest concentration of PFOS (30.9 ng/l) was observed at location YK1, which is located in the Daliao River, a main tributary of the Liaohe River system adjacent to the city of Yingkou. 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 (Zhang et al., 2009). The watershed encompasses a number of densely industrialized zones with machinery, electronics, metal refining, and petroleum and chemical industries.

Compared to other research findings for China, concentrations of PFCs in waters from estuarine and coastal areas of northern Bohai Sea were greater than those from the Pearl River Delta, where the first study of PFCs in China was conducted, and the Chongqing, Yichang, Dongguan, Wuhan, Nanjing, and Beijing regions (Jin, 2006; So et al., 2007; So et al., 2004; Zhao et al., 2007) (Table 3). Moreover, it has been reported that PFOS and PFOA concentrations around the city of Dalian from coastal areas of the Bohai Sea were less than those found in the present study as well, ranging from nd to 2.25 ng/l and from 0.170 to 37.6 ng/l, respectively (Ju et al., 2008).

In general, PFOS and PFOA concentrations in waters from estuarine and coastal areas of northern Bohai Sea were consistent with

Fig. 2. Spatial distributions and relative contributions of individual PFCs to total (%) in water from north Bohai Sea.

Table 2

Overview of PFCs analysis results for water, sediment, soil, and biologic samples collected from north Bohai Sea.

Compounds	Water	Sediment	Soil	Biologic
Sampling location (n)	36	35	31	25
Samples analyzed (n)	36	35	31	42
Samples detected	n(%)			
PFBS	0(0)	0(0)	0(0)	3(7)
PFHxS	0(0)	0(0)	0(0)	0(0)
PFOS	12(33)	3(9)	2(6)	20(48)
PFDS	0(0)	0(0)	0(0)	2(5)
PFBA	23(64)	0(0)	0(0)	16(38)
PFHxA	22(61)	4(11)	0(0)	9(21)
PFHpA	32(89)	1(3)	0(0)	1(2)
PFOA	21(58)	3(9)	9(26)	11(26)
PFNA	3(8)	13(37)	15(43)	1(2)
PFDA	5(14)	2(6)	1(3)	33(78)
PFUnA	3(8)	16(46)	11(31)	7(17)
PFDoA	0(0)	0(0)	0(0)	0(0)
Average detected	10(28)	4(11)	3(10)	9(21)

the results of previous studies (Table 3). Concentrations observed in the present study were greater than those found in most rivers of Japan and much greater than those found offshore of Japan and oceanic samples including the Western Pacific Ocean, Central to Eastern Pacific Ocean and North Atlantic Ocean (Yamashita et al., 2005). Concentrations of PFOS and PFOA were either comparable to or less than those detected in coastal waters of South Korea (Naile et al., 2010; Rostkowski et al., 2006), Yodo River Basin, Japan (Lein et al., 2008) and various river and coastal waters in Brazil (Quinete et al., 2009). Concentrations of PFOS and PFOA measured in this study were similar to those reported for Tokyo Bay, Japan (Sakurai et al., 2010; Yamashita et al., 2004). In the present study, the maximal concentrations of PFOS (30.9 ng/l) and PFOA (81.7 ng/l) were measured in Liaodong Bay, which were less than the greatest concentrations of PFOS (123 ng/l) and PFOA (2600 ng/l) measured in the Yodo River Basin, which is one of the most polluted rivers in Japan.

Although PFOS and PFOA were the dominant PFCs found in water samples in the present study, PFBA, PFHxA and PFHpA were detected in approximately 70% of the samples analyzed at concentrations greater than the LOQ, but the concentrations of these PFCs were less than those of PFOS and PFOA. Concentrations of PFBA, PFHxA and PFHpA ranged from <LOQ to 74.1 ng/l, <LOQ to 2.32 ng/l, and <LOQ to 34.5 ng/l, with a means of 3.44 ng/l, 1.19 ng/l, and 2.85 ng/l, respectively. This indicates that other PFCs, in addition to PFOS and PFOA, should be considered in future monitoring and risk assessment. However, it should be noted that the reported concentrations of waterborne PFCs were based on a single survey, thus temporal variations could not be addressed at this time. Further studies would be conducted to look at monthly or seasonal variations in PFCs concentrations in these areas.

As sediments are considered to be the ultimate sinks and reservoirs of many contaminants, information about sediment contamination is essential in the assessment of the impact of human activities on aquatic systems. Concentrations of PFCs in sediments from the estuarine and coastal areas of north Bohai Sea were generally less than the corresponding MDLs. Total concentrations of PFCs ranged from <LOQ to 4.31 ng/g dw with a mean of 0.622 ng/g dw. PFOS and PFOA were the dominant PFCs with concentrations that ranged from <LOQ to 1.97 ng/g dw with a mean of 1.67 ng/g dw and from <LOQ to 0.542 ng/g dw with a mean of 0.298 ng/g dw, respectively (Fig. 3). Concentrations of the other ten target analytes were less than their respective LOQs at most of the sampling locations except for PFNA and PFUnA. Concentrations of PFOS were greater than those of PFOA at all locations where they were detected.

The greatest concentrations of PFOA (0.542 ng/g dw) and second greatest concentration of PFOS (1.55 ng/g dw) were observed in sediments from QH2, and considerably elevated concentration of PFOS (1.48 ng/g dw) was found in the same vicinity (QH3). These sites, located at the mouth of the Tang River Estuary, close to a sewage outfall and industrial discharge, reflected a potential pollution source of PFOS and PFOA from Qinhuangdao City. Furthermore, the greatest concentration of PFOS (1.97 ng/g dw)

Table 3

Comparison of PFOS and PFOA concentrations (ng/l) in water with other studies in these adjacent areas.

Location		PFOS	PFOA	Reference
China	Estuarine and coastal areas of north Bohai Sea	nd–30.9	2.58–81.7	This study
	Coastal area of China	0.02–9.68	0.24–15.3	Yamashita et al., 2005
	Beijing	1.75–4.09	5.51–7.85	Zhao et al., 2007
	Dongguan	0.90–99	0.85–4.4	So et al., 2007
	Chongqing	nd–0.35	nd–35	So et al., 2007
	Yichang	0.29–0.61	4.1–4.9	So et al., 2007
	Wuhan	2.3–5.3	2.8–5.6	Jin et al.,2006
	Nanjing	0.33–0.38	2.1–2.4	So et al., 2007
	Shanghai	0.62–14	22–260	So et al., 2007
	Pearl river delta	0.02–12	0.24–16	So et al., 2004
	Dalian coast	nd–2.25	0.17–37.6	Ju et al., 2008
	Hong Kong	0.09–3.1	0.73–5.5	So et al., 2004
Japan	Tokyo Bay	12.7–25.4	154–192	Yamashita et al., 2004
	Tokyo Bay	0.78–17	2.7–63	Sakurai et al., 2010
	Survey of Japan	0.89–5.73	0.97–21.5	Saito et al., 2003
	Yodo river basin	0.4–123	4.2–2600	Lein et al., 2008
	Kyoto	7.9–110	5.12–10	Senthilkumar et al., 2007
	Offshore of Japan	0.04–0.07	0.14–1.06	Yamashita et al., 2005
South Korea	Coastal area of Korea	0.04–2.53	0.24–11.4	Yamashita et al., 2005
	West and South coasts of Korea	0.04–730	0.24–320	So et al., 2004
	West coasts of Korea	4.11–450	2.95–68.6	Naile et al., 2010
	Gyeonggi Bay	2.24–651	0.9–62	Rostkowski et al., 2006
Ocean	Western Pacific ocean	0.054–0.078	0.136–0.142	Yamashita et al., 2005
	Central to Eastern Pacific ocean	0.001–0.020	0.015–0.062	Yamashita et al., 2005
	North Atlantic ocean	0.009–0.036	0.160–0.338	Yamashita et al., 2005

nd = not detectable, means concentration less than corresponding LOQs.

Fig. 3. Spatial distributions of PFCs in sediments from north Bohai Sea.

and relatively great concentration of PFOA (0.305 ng/g dw) were found in riverine sediment from the Jinzhou area (JZ4). This was also an area where some of the greatest PFCs concentrations were observed in water.

Compared to previous studies, concentrations of PFOS in sediments from the estuarine and coastal areas of the northern Bohai Sea were similar to those from the Zhujiang River, China ($< \text{LOQ} - 3.10 \text{ ng/g dw}$) (Bao et al., 2010) and four rivers by San Francisco Bay, USA ($< \text{LOQ} - 1.30 \text{ ng/g dw}$) (Higgins et al., 2005), but less than those from the Kyoto River, Japan ($< \text{LOQ} - 11.0 \text{ ng/g dw}$) (Senthilkumar et al., 2007). The maximum concentration of PFOS in sediments (1.97 ng/g dw) in the present study was greater than those reported from the Daliao River system, China ($< \text{LOQ} - 0.37 \text{ ng/g dw}$) (Bao et al., 2009), the Huangpu River, China ($< \text{LOQ} - 0.46 \text{ ng/g dw}$) (Bao et al., 2010), the tidal flat areas of Ariake Sea, Japan (0.09–0.14 ng/g dw) (Nakata et al., 2006), and the Roter Main River, Germany (0.07–0.31 ng/g dw) (Becker et al., 2008).

Concentrations of PFOA in sediments of this watershed were greater than those of the Daliao River system, China (nd – 0.17 ng/g dw) (Bao et al., 2009) and the Roter Main River, Germany (0.02–0.07 ng/g dw) (Becker et al., 2008), comparable to those from the Huangpu River (0.20–0.64 ng/g dw) and the Zhujiang River (0.09–0.29 ng/g dw), China (Bao et al., 2010), and San Francisco Bay, USA (0.16–0.23 ng/g dw) (Higgins et al., 2005), whereas they were less than those of the Kyoto River ($< \text{LOQ} - 3.9 \text{ ng/g dw}$) (Senthilkumar et al., 2007) and the Ariake Sea, Japan (0.84–1.1 ng/g dw) (Nakata et al., 2006). Overall, concentrations of PFOA observed in sediments during the present study varied widely, which indicates multiple sources across the estuarine and coastal areas of the northern Bohai Sea.

Concentrations of PFCs in wildlife are given in Table 4. PFOS was greater than the LOQ in 67% of all biologic samples taken from the estuarine and coastal areas of the northern Bohai Sea and PFOS was found to be the most frequently detected PFC (Table 2). Concentrations of PFOS in fish, loach, shrimp, clam, crab, frog, and snail were 262 ng/g dw, 44.5 ng/g dw, 14.0 ng/g dw, 5.72 ng/g dw, 2.64 ng/g dw, nd, and $< \text{LOQ}$, respectively. This indicates the greatest accumulation in organisms at the top of the food web, such as fish. Concentrations of PFOA in biota were less than those of PFOS, with

Table 4

Concentrations (ng/g dw) of PFCs in biologic samples from north Bohai Sea.

Compounds	Fish	Crab	Shrimp	Clam	Frog	Snail	Loach
No. of samples	13	14	3	6	2	2	2
PFOS	262	2.64	14.0	5.72	nd	nd	44.5
PFOA	nd	1.45	2.26	nd	nd	nd	0.790
PFHxA	0.692	0.242	nd	1.16	2.90	nd	1.00
PFDA	1.18	1.21	0.918	0.705	4.01	nd	1.25
PFUnA	0.258	0.433	nd	1.37	nd	nd	nd
PFBA	1.37	1.66	nd	1.11	1.07	nd	nd
PFCs	265	7.63	17.2	10.1	7.97	nd	47.5

a detection rate of only 26%. Corresponding, the concentrations of PFOA in shrimp, crab, loach, fish, clam, frog, and snail were 2.26 ng/g dw, 1.45 ng/g dw, 0.790 ng/g dw, nd, nd, nd, and nd, respectively.

Considering that fish and crabs are among the most abundant organisms in this area and were collected from almost all sub-regions of sampling areas, the six most commonly detected PFCs in those organisms were further analyzed (Fig. 4). PFOS was the predominately detected PFC in fish, ($n = 25$) throughout the study area, with quantifiable concentrations ranging from 0.86 ng/g dw at TS (Tangshan) to 791 ng/g dw at DD (Dandong). Fish collected from DL (Dalian) and YK (Yingkou) contained greater concentrations of PFOS (238 ng/g dw and 573 ng/g dw) as well. PFOS, PFOA and PFDA were detected in most samples of crab, but concentrations were less and there was little variation among concentrations of target PFCs. PFOS concentrations in crabs ranged from $< \text{LOQ}$ at YK and QH (Qinhuangdao) to 8.73 ng/g dw at TS, and the second greatest concentration (7.17 ng/g dw) in crabs was from DD. This concentration was similar to that observed in fish, which indicates possible sources near Dandong City. The greatest concentration of PFOA (3.13 ng/g dw) and PFDA (0.945 ng/g dw) were observed in crabs from TS.

Greater concentrations of PFOS in fish were observed in the eastern part of the northern Bohai Sea (Fig. 4), with a mean of 534 ng/g dw. This concentration was comparable to those observed previously in South Korea, Japan, Brazil, and Germany (Becker

et al., 2010; Naile et al., 2010; Nakata et al., 2006; Quinete et al., 2009; Taniyasu et al., 2003; Yoo et al., 2009), but generally greater than those previously reported in China, the North American Great Lakes, and Netherlands (Boulanger et al., 2004; Delinsky et al., 2010; Gulkowska et al., 2006; Kwadijk et al., 2010; Shi et al., 2010). These locations have been subjected to anthropogenic influences as a result of rapid urbanization and industrialization. Overall, they seemed to be influenced primarily by domestic sewage and industrial effluent from the nearby areas of highly urbanized and industrialized zones of Yingkou, Dalian and Dandong cities.

PFCs have been reported at greater concentrations in urban areas than in the rural areas, which indicates that in addition to industrial activities urban areas are also the sources of PFCs (Kim and Kannan, 2007; Nakata et al., 2006; Saito et al., 2003; Taniyasu et al., 2003). Releases from various PFCs sources not only contaminate water systems but also contaminate soils. For example, PFOS and PFOA can absorb onto sediment and sludge (Hansen et al., 2002; Higgins et al., 2005; Sinclair and Kannan, 2006), therefore, soils could be another sink for PFCs. Previous studies have reported concentrations of PFCs in water, sediment and biologic samples,

Fig. 4. Spatial distribution and compositional patterns of PFCs detected in fish and crabs from different areas along north Bohai Sea.

however, few have reported the occurrence, distribution, sources and risks of PFCs in soils (Naile et al., 2010).

Spatial distribution of 12 PFCs in soils was generated by using ArcGis software (ESRI, US), and an interpolation method of Ordinary Kriging was adopted for the interpolation of geographic data (Fig. 5). In the estuarine and coastal areas of northern Bohai Sea, concentrations of PFCs in soils were generally less than the LOQ. Only two sites contained detectable concentrations of PFOS and nine sites contained PFOA greater than the LOQ. However, PFNA and PFUnA were found at a relatively great rate of occurrence with

43% and 31%, respectively (Table 2), which was the similar case in the distribution of sedimentary PFCs. Total concentrations of PFCs were in the range of < LOQ–1.72 ng/g dw with a mean of 0.579 ng/g dw. Concentrations of PFOS and PFOA in soils ranged from < LOQ to 0.702 ng/g dw with a mean of 0.582 ng/g dw and from < LOQ to 0.473 ng/g dw with a mean of 0.210 ng/g dw, respectively (Fig. 5). While concentrations of the other two routinely found PFCs of PFNA and PFUnA were comparable, ranging from < LOQ to 0.701 ng/g dw with a mean of 0.281 ng/g dw and from nd to 0.421 ng/g dw with a mean of 0.259 ng/g dw, respectively. There

Fig. 5. Spatial distributions of PFCs in soils from north Bohai Sea.

Fig. 6. Comparison of PFOS in water from north Bohai Sea with suggested water quality criteria values for the protection of aquatic organisms (CMC: criteria maximum concentration; CCC: criteria continuous concentration), field-based bioconcentration factors (BCF) given as well.

did not seem to be a significant difference in the amount of PFCs accumulation between soils and sediments, as neither had a PFOS and PFOA concentration greater than 2.0 ng/g dw, however.

Concentrations of PFCs in soils exhibited a spatial pattern that was different from that in sediments. The greatest concentrations were observed at HL5, which is adjacent to the city of Huludao. The greatest concentration of PFOA (0.473 ng/g dw) and the second greatest concentration of PFOS (0.463 ng/g dw) were observed at the same site while the greatest PFOS was found at YK3, which is located in the Daliao River adjacent to the city of Yingkou. This was also where the greatest PFOS (30.9 ng/l) was observed in water. This suggested possible input from soil to surface waters. In general, soils and sediments in the estuarine and coastal areas of the northern Bohai Sea contain only small amounts of PFCs. In terms of matrix-dependent accumulation of PFCs, the results of the present study were similar to those observed previously in South Korea (Naile et al., 2010).

Mean concentrations of PFOS in water from eight sub-regions were used to calculate field-based bioconcentration factors (BCF) for fish in the estuarine and coastal areas of the northern Bohai Sea. A field-based BCF was defined as the concentration in fish divided by the concentration in water. The mean BCF values for fish were 3,100 with a maximum value of 85,000 at Dalian and a minimum value of 450 at Tangshan with corresponding log BCF values of 2.7–4.9 (Fig. 6). The BCF values found in the present study were comparable to BCF values reported by Taniyasu et al. (log BCF of 2.4–4.6) in Japan (Taniyasu et al., 2003) and Martin et al. (log BCF of 3.0) for their laboratory study of rainbow trout (Martin et al., 2003), but are less than those reported previously in west coastal of Korea (log BCF of 3.2–5.1) and in Etobicoke Creek, Ontario following a spill of AFFF (log BCF of 3.8–5.1) (Moody et al., 2002; Naile et al., 2010). Calculation of log BCF values for PFOA was not possible due to the lack of data for biota. Concentrations of PFOA were less than the limit of quantification in nearly all fish samples. Thus, it can be concluded that PFOA was not bioaccumulated in fish, and this phenomenon was in good agreement with previous studies (Martin et al., 2003; Naile et al., 2010; Quinete et al., 2009; Yeung et al., 2009).

An evaluation of the ecological risk to aquatic animals associated with exposure to PFOS was performed by comparing concentrations in water with water quality values (Giesy et al., 2010; Yoo et al., 2009). Concentrations of PFCs measured in waters around the northern Bohai Sea (all ng/l level) did not approach the numerical water quality criteria (all > several µg/l). Concentrations of PFOS were less than both the criteria maximum concentration (CMC = 21 µg/l) or criteria continuous concentration (CCC = 5.1 µg/l) values, as well as avian wildlife values (AWV = 17 ng/l) (Fig. 6).

While the results of this study indicate little potential for risk, based on concentrations measured in water, risk of environmental exposure to PFCs cannot be neglected because the accumulation mechanisms and exposure routes of PFCs are different than that of more hydrophobic persistent organic pollutants, such as PCBs and dioxins. More toxicological and environmental exposure data are needed to address the effects this class of compounds has on environmental systems (Beach et al., 2006). Also, to make comparisons between concentrations in organisms associated with adverse effects, concentration in the blood, liver and/or eggs of birds would be necessary since these are the only values available for which to calculate toxicity reference values (TRVs) (Newsted et al., 2006, 2008; Newsted et al., 2007; Newsted et al., 2005; Yoo et al., 2008).

As part of an ongoing study to determine PFCs concentrations, distributions, sources and environmental fates in the Bohai Sea and Yellow Sea ecosystem, the present study has provided baseline data on PFCs concentrations in water, sediment, soil, and biota col-

lected from the estuarine and coastal areas of the northern Bohai Sea. The current findings should help researchers better understand the geographic distributions and extent of PFCs contamination in the estuarine and coastal areas of the Yellow Sea ecoregion including the northern portions of the Bohai Sea. Further detailed work with a more intensive sampling effort with temporal discrimination is recommended to identify any shifts in production to shorter chained or lesser fluorinated PFCs. Such approach will help to elucidate status of trends and source identification, and allow evaluation of control measures to reduce riverine discharge of PFCs into the coastal and marine ecosystem.

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