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Perfluorinated compounds in water and sediment from coastal regions of the northern Bohai Sea, China

Chunli Chen^{a,b}, Tiewu Wang^a, Jong Seong Khim^c, Wei Luo^a, Wentao Jiao^{a,b}, Yonglong Lu^{a,*}, Jonathan E. Naile^d, Wenyu Hu^{a,b}, Xiang Zhang^{a,b}, Jing Geng^{a,b}, Cencen Bi^{a,b}, Jing Li^{a,b} and John P. Giesy^{d,e}

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Concentrations of perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA) and other perfluorinated compounds (PFCs) were measured in water and sediment from coastal Bohai Bay and surrounding rivers flowing into the bay. Of the 15 PFCs measured, PFOS and PFOA were detected with the greatest frequency. Concentrations in water ranged from <0.2 to $31 \text{ ng}\cdot\text{L}^{-1}$ and <1.0 to $82 \text{ ng}\cdot\text{L}^{-1}$ for PFOS and PFOA, respectively. Concentrations of PFOS and PFOA in sediments ranged from <0.1 to $2.0 \text{ ng}\cdot\text{g}^{-1}$ dw and <0.1 to $0.5 \text{ ng}\cdot\text{g}^{-1}$ dw, respectively. Concentrations of PFCs in Bohai Bay were less than those observed in other areas in Asia, but greater concentrations of Σ PFCs were observed in the Dalin River with concentrations increasing from upstream to downstream, and the greatest concentrations in sediment were observed in tidal flats. The ratio of Σ PFCs in sediment and water indicated that sediment could serve as a significant sink for PFUNA.

Keywords: perfluorooctane sulfonate (PFOS); perfluorooctanoic acid (PFOA); marine and fresh water environment; river; source

1. Introduction

Per- and poly-fluorinated compounds (PFCs) are a group of persistent organic pollutants (POPs) that were produced for over 50 years but have only recently been recognised as global contaminants [1–3]. Owing to their unique amphiphilic properties as well as their persistence and bioaccumulation potential [4], they have been widely distributed in the global environment [5,6]. Despite studies on contaminants such as polycyclic aromatic hydrocarbons (PAHs), dichlorodiphenyl-trichloroethane (DDT) and polychlorinated biphenyls (PCBs) in China, particularly in the northern Bohai Sea [7–9], relatively little is known about the current status of PFCs in this commercially

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important Chinese coastal region [10–12]. Sediments and the deep oceans have been suggested as the two final sinks of PFCs [13,14], and some PFCs such as perfluorooctanesulfonate (PFOS) have been reported to be sorbed to solids [14–17]. Despite the widespread occurrence and distribution of PFCs in water and biota, relatively little is known about concentrations of PFCs in sediments. This is particularly true with respect to the coastal and marine environment, especially in China. Until now, there has been little information on concentrations of PFCs in water or sediment of the Bohai Sea and its tributaries [18]. The coastal regions of the North Bohai Sea (NBS) are a major commercial transportation route and constitute a region of significant urbanisation and industrialisation of China [19].

The goal of the present study was to determine the occurrence, distribution and sources of selected PFCs in water and sediments from the rivers that empty into the Bohai Sea and coastal and marine regions of Bohai Bay. In addition, the relationship between waterborne and sedimentary PFCs was studied.

2. Materials and methods

2.1. Sampling location and sample preparation

The NBS is located in northeast China, along the provinces of Hebei and Liaoning. This is an intensely developed region with an area of $7.9 \times 10^4 \text{ km}^2$, which makes up $\sim 7\%$ of the land area of the Bohai Rim. Coastal regions of the NBS have a warm temperate continental monsoon climate, with an average annual temperature of 11°C , relative humidity of 68% and a mean annual precipitation of $5.8 \times 10^2 \text{ mm}$.

In May 2008, 34 water samples and corresponding surficial sediments were collected from the outlets of rivers and creeks in coastal regions of the NBS (Figure 1). The drainage areas of these

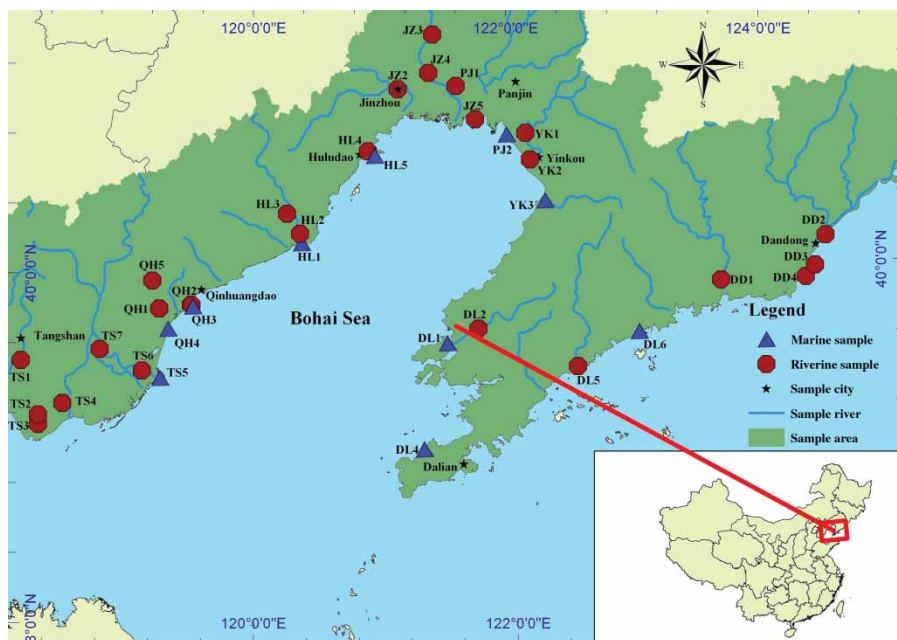


Figure 1. Sampling sites in coastal cities of China along Bohai Bay: Tangshan (TS), Qinquangdao (QH), Huludao (HL), Jinzhou (JZ), Panjin (PJ), Yingkou (YK), Dalian (DL) and Dandong (DD).

rivers are the important agricultural and chemical production areas [20]. Throughout the survey, a global positioning system (GPS) was used to locate the sampling sites. Surficial sediments (top 1–10 cm) were collected using a trowel from the bed close to the bank. Representative samples were prepared by mixing five subsamples from the area of $\sim 5 \text{ m}^2$. Samples were stored on ice for transport to the laboratory. All equipment was pre-cleaned with distilled water and methanol, and rinsed with water from the sampling location before sample collection. Samples were stored frozen until extraction. Sediments were dried and then homogenised with a mortar and pestle and passed through a 2.0 mm sieve to remove pebbles and debris.

2.2. Standards and reagents

A mixture of different perfluorinated compounds (PFCs-mix, >98%, Wellington Laboratories) including PFOS, perfluorooctanoic acid (PFOA), perfluorobutyric acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTriDA), perfluorotetradecanoic acid (PFTeDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS) and perfluorodecane sulfonate (PFDS), each at a concentration of $6.0 \text{ ng}\cdot\text{mL}^{-1}$, was used as an external standard, whereas 0.5 mL of PFOS [$^{18}\text{O}_2$] and PFOA [$1,2,3,4^{13}\text{C}$] (RTI International) at $5.0 \text{ ng}\cdot\text{mL}^{-1}$ were used as internal standards. Methanol (HPLC grade), acetic acid (analytical grade) and nitrogen gas (> 99.9995% purity) were used. Milli-Q water was obtained from a Milli-Q Gradient A-10 (Millipore, Bedford, MA, USA).

2.3. Sample extraction and clean-up

2.3.1. Water

Water was extracted using Oasis HLB solid-phase cartridges (0.2 g, 6 mL) (Waters Corp., Milford, MA) as previously reported [21]. Cartridges were pre-conditioned by passing 10 mL of 100% methanol followed by 10 mL nano-pure water at a rate of 1 drop per second. A 500 mL sample of water was spiked with the internal standard (isotopically labeled PFOS and PFOA), and loaded onto cartridges at a rate of 1 drop per second. The column was washed with 5 mL of 40% methanol in water at a rate of 1 drop per second, and the column was allowed to dry for at least 2 h prior to elution. PFCs were eluted with 10 mL of methanol at a rate of 1 drop per second. Samples were collected in a polypropylene centrifuge tube, and were reduced to 1 mL under a gentle stream of high-purity nitrogen. After passing through a nylon membrane Millex filter unit (pore diameter $0.2 \mu\text{m}$, Whatman, Maidstone, UK), extracts of water samples were transferred to glass auto-sampler vials for instrumental analysis.

2.3.2. Sediment

Perfluorinated compounds in sediments were analysed using methods similar to those that have been published previously [16]. Approximately 1.0 g dry sediment was weighed and placed in a clean 50 mL polypropylene tube, with PFOS [$^{18}\text{O}_2$] and PFOA [$1,2,3,4^{13}\text{C}$] and 10 mL of 1% acetic acid. The resulting slurry was then mixed in a sonication bath at 60°C for 15 min. The tube was centrifuged at 3000 rpm for 3 min and the acetic acid solution was then decanted into a second 50 mL tube; 2.5 mL of 90% methanol and 10% (V/V) 1% acetic acid solution was added to the original tube. The sample was again mixed using a vortex mixer and sonicated for 15 min at 60°C . The sample was centrifuged and decanted as before. This process was repeated once more

and a final 10 mL of 1% acetic acid wash was performed. All extracts were combined to make a final volume of ~35 mL before being passed through the SPE cartridge in a similar fashion as was described above in the water extraction procedure.

2.4. HPLC-MS-MS conditions

Analytical methods were optimised to allow for simultaneous detection of all target analytes. Analyte separation was accomplished by use of an Agilent 1200 HPLC fitted with a Thermo Scientific Betasil C18 (100 × 2.1 mm, 5 μm particle size) analytical column operated at 35 °C. Gradient conditions were a flow rate of 300 μL·min⁻¹, 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 until 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.

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

2.5. Quantification and quality assurance

One of the major limitations of trace-level analysis of PFCs, such as PFOS and PFOA, is background contamination [22,23]. In order to ensure the accuracy of the sampling, extraction and analytical procedures, field blanks were conducted with each set of water samples analysed. Procedural blanks and recoveries were determined for each set of extractions. Quantification was performed using the internal standard method based on ¹⁸O₂-PFOS and ¹³C₄-PFOA as the surrogate.

Quantitative analyses were performed with high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). To minimise interferences from the instrument, a guard column was placed just ahead of the injection port to isolate the peaks for the background contamination from the analytical peaks of interest [24]. The limit of detection (LOD) was defined as three times the signal to noise ratio of the least concentration, and the limit of quantification (LOQ) was defined as three times the LOD value. The accuracy (% recovery) and precision (pooled coefficient of variation) were estimated by replicate analysis for three concentrations. The accuracy was determined to be within 20%, whereas the precision, expressed as the coefficient of variation, was also <20%. All the target compounds in water and sediment samples that were detected in the procedural blanks were less than the LOQ. Field blank levels in water samples were found only for PFPeA, at a concentration ranging from not detected (ND) to 3.1 ng·L⁻¹, and those sample sets that were found to have notable contamination in field blanks were eliminated from further analysis. The detection limits and the recoveries for the compounds analysed in the various matrices are summarised (Table 1).

Total organic carbon (TOC) and total nitrogen (TN) were analysed by Universal CHNOS Elemental Analyzer (Elementar Vario EL III, Germany). Soil pH was measured (10 g of air-dried soil suspended in 25 mL deionised water) using a pH meter.

Table 1. Limits of detection (LOD), limits of quantification (LOQ), method detection limits (MDL) and recovery of PFCs from water or sediment.

Chemical	LOD		LOQ		MDL		Recovery (%)	
	Water (ng·mL ⁻¹)	Sediment (ng·g ⁻¹)	Water (ng·mL ⁻¹)	Sediment (ng·g ⁻¹)	Water (ng·L ⁻¹)	Sediment (ng·g ⁻¹)	Water	Sediment
PFBS	0.1	1.0	0.5	1.0	1.0	1.0	93.7	32.0
PFHxS	0.1	0.1	0.1	0.5	0.2	0.5	136	134
PFOS	0.1	0.1	0.1	0.5	0.2	0.5	101	94.6
PFDS	0.1	0.1	0.1	0.5	0.2	0.5	101	43.4
PFPeA	1.0	1.0	1.0	1.0	2.0	1.0	NA	NA
PFHxA	0.1	0.1	0.5	0.1	1.0	0.1	84.6	78.5
PFHpA	0.1	0.1	0.5	0.1	1.0	0.1	103	123
PFOA	0.1	0.1	0.5	0.5	1.0	0.5	88.0	89.1
PFNA	1.0	1.0	1.0	1.0	2.0	1.0	132	135
PFDA	0.1	0.1	0.1	0.1	0.2	0.1	93.2	106
PFUnA	1.0	0.1	1.0	0.5	2.0	0.5	112	53.4
PFDoA	1.0	0.1	1.0	0.1	2.0	0.1	76.7	70.2
PFTrDA	1.0	1.0	1.0	1.0	2.0	1.0	NA	NA
PFTeDA	1.0	1.0	1.0	1.0	2.0	1.0	NA	NA

Notes: NA, no standard was spiked. PFOS, perfluorooctanesulfonate; PFOA, perfluorooctanoic acid; PFBA, perfluorobutyric acid; PFPeA, perfluoropentanoic acid; PFHxA, perfluorohexanoic acid; PFHpA, perfluoroheptanoic acid; PFNA, perfluorononanoic acid; PFDA, perfluorodecanoic acid; PFUnA, perfluoroundecanoic acid; PFDoA, perfluorododecanoic acid; PFTDA, perfluorotridecanoic acid; PFTeDA, perfluorotetradecanoic acid; PFBS, perfluorobutane sulfonate; PFHxS, perfluorohexane sulfonate; PFDS, perfluorodecane sulfonate.

3. Results and discussion

3.1. PFCs distribution in water and sediment samples

3.1.1. PFCs in water

Concentrations of 15 target PFCs in water from coastal regions of the Bohai Sea were measured (Table 2). However, concentrations of PFCs in water from coastal regions of NBS were frequently not detectable, and PFHxA, PFBS, PFHxS, PFDS and PFTeDA were less than their respective LOQ in water. PFOS was detected in 34% of waters. There was a relatively large amount of variation in concentrations among and within sampling regions. Concentrations of PFOS at locations YK1 (midstream of the Daliao River), DD1 (the Dayang River) and DD3 (downstream of Yalu River) were greater than those at any other locations, with the maximum concentration of 30 ng PFOS·L⁻¹ found at location YK1, which was midstream in the Daliao River. The water quality criterion (WQC) that was calculated to be protective for avian wildlife was estimated to be 47 ng PFOS·L⁻¹ [25], which was slightly greater than even the greatest concentration of PFOS in water.

The rate of detection of PFOA in water from coastal regions of the NBS was 51%, but concentrations of PFOA were near the method detection limit (MDL). Concentrations of PFOA at locations JZ3 (upstream of the Dalin River), JZ4 (midstream of the Dalin River) and JZ5 (downstream portions of the Dalin River) were greater than those at other sites from coastal regions of the NBS. The maximum concentration of 82 ng PFOA·L⁻¹ was observed at location JZ5, which was downstream in the Dalin River.

PFHpA was the prevalent perfluorocarboxylic acid (PFCA) in waters from coastal regions of the NBS (Table 2). Concentrations of PFHpA ranged from <1.0 to 34 ng·L⁻¹, with a maximum concentration observed at JZ5 (downstream of the Dalin River). Conversely, PFNA, PFDA and PFPeA were not detected in water from most locations, and were detected at relatively small concentrations in water from some locations such as DD1 (the Dayang River) and DD3 (downstream of the Yalu River) and YK1 (midstream of the Daliao River). Concentrations of PFPeA ranged

Table 2. Perfluorinated compound concentrations (ng·L⁻¹) in waters collected from the Bohai Sea, northern China.

ID	PFASs			PFCAs		
	PFOS	PFOA	PFHpA	PFNA	PFDA	PFPeA
DD1	9.2	6.6	0.9	8.0	10	<2.0
DD2	<0.2	<1.0	< 1.0	<2.0	<0.2	<2.0
DD3	12	2.1	1.6	1.5	4.0	<2.0
DD4	<0.2	<1.0	<1.0	<2.0	<0.2	<2.0
DL1	<0.2	<1.0	<1.0	<2.0	<0.2	<2.0
DL2	<0.2	<1.0	1.8	<2.0	<0.2	<2.0
DL4	<0.2	<1.0	2.3	<2.0	<0.2	<2.0
DL5	<0.2	<1.0	2.2	<2.0	<0.2	2.3
DL6	4.0	<1.0	1.1	<2.0	<0.2	2.1
TS1	<0.2	5.5	1.6	<2.0	<0.2	<2.0
TS2	<0.2	2.4	1.3	<2.0	<0.2	<2.0
TS3	<0.2	2.4	1.2	<2.0	<0.2	<2.0
TS4	<0.2	3.3	1.0	<2.0	<0.2	<2.0
TS5	<0.2	<1.0	<1.0	<2.0	<0.2	<2.0
TS6	1.9	4.8	3.3	<2.0	<0.2	<2.0
HL1	<0.2	<1.0	<1.0	<2.0	<0.2	<2.0
HL2	<0.2	<1.0	<1.0	<2.0	<0.2	<2.0
HL3	<0.2	<1.0	1.1	<2.0	<0.2	<2.0
HL4	3.7	9.0	<1.0	<2.0	<0.2	<2.0
HL5	<0.2	2.6	1.7	<2.0	<0.2	2.2
JZ2	<0.2	2.9	<1.0	<2.0	<0.2	<2.0
JZ3	4.5	68	1.4	<2.0	0.46	<2.0
JZ4	<0.2	72	2.9	<2.0	<0.2	<2.0
JZ5	<0.2	82	34	<2.0	<0.2	<2.0
PJ1	<0.2	7.8	2.7	<2.0	<0.2	<2.0
PJ2	6.7	7.6	2.9	<2.0	0.64	<2.0
QH1	<0.2	<1.0	1.1	<2.0	<0.2	<2.0
QH2	<0.2	1.6	3.9	<2.0	<0.2	<2.0
QH3	2.8	<1.0	2.0	<2.0	<0.2	<2.0
QH4	<0.2	<1.0	<1.0	<2.0	<0.2	<2.0
QH5	4.6	<1.0	1.6	<2.0	<0.2	<2.0
YK1	31	3.5	1.6	<2.0	5.7	<2.0
YK2	1.4	11	11	<2.0	<0.2	2.3
YK3	<0.2	<1.0	<1.0	<2.0	<0.2	<2.0
Mean	2.5	8.9	2.7	<2.0	0.7	<2.0
SD	5.8	21	5.8	<2.0	2.0	<2.0
Median	<0.2	1.8	1.4	<2.0	<0.2	<2.0
Geometric mean	0.4	2.0	1.4	<2.0	0.2	<2.0
Geometric SD	6.6	4.8	2.5	1.4	3.3	1.3

Notes: Concentrations less than method detection limit (MDL) were assumed to be half the MDL for statistical purposes. PFCA, perfluorocarboxylic acid; PFAS, perfluoroalkyl sulfonate; PFOS, perfluorooctanesulfonate; PFOA, perfluorooctanoic acid; PFPeA, perfluoropentanoic acid; PFHpA, perfluoroheptanoic acid; PFNA, perfluorononanoic acid; PFDA, perfluorodecanoic acid.

from <2.0 to 2.3 ng·L⁻¹, with the greatest concentration observed at location YK2, which was downstream in the Daliao River.

Total concentrations of perfluoroalkyl sulfonates (PFASs) and PFCAs in water were compared among locations (Figure 2). The greatest concentrations of PFCAs in decreasing order were observed in water from locations JZ5 (downstream of the Dalin River), followed by JZ4 (midstream of the Dalin River), JZ3 (upstream of the Dalin River) and DD1 (the Dayang River). Samples from YK1 (midstream of the Daliao River) contained the greatest concentrations of PFASs. The patterns of relative proportions that PFASs and PFCAs contributed to \sum PFCs indicates that sources of PFCs were different among cities [11], and possible point sources of PFCAs could be located at these locations.

Total concentrations of PFCs (\sum PFCs) in water ranged from ND to 1.2×10^2 ng·L⁻¹, with \sum PFCs at location JZ3 (upstream of the Dalin River), JZ4 (midstream of the Dalin River) and JZ5

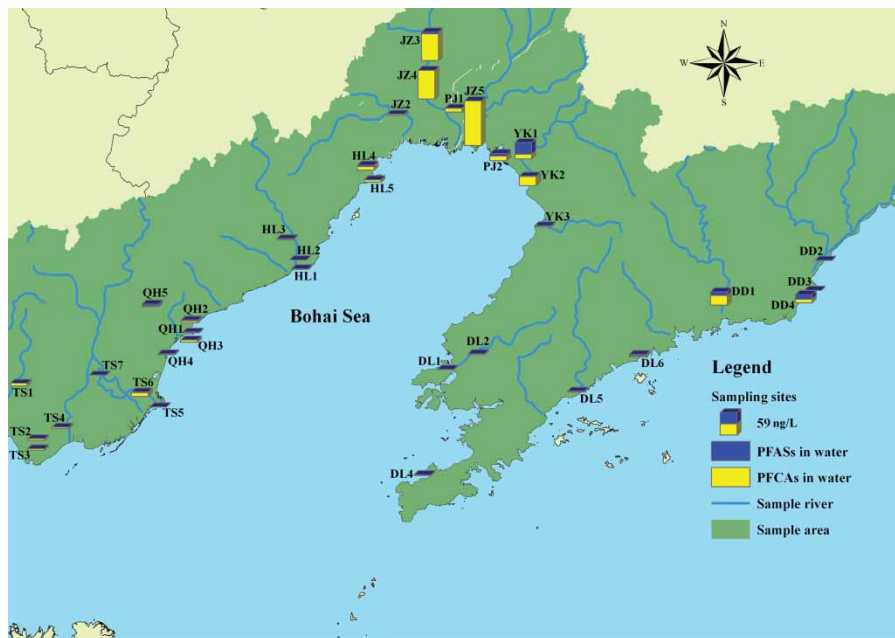


Figure 2. Comparison of total concentrations of PFCAs and PFASs in water samples among locations ($\text{ng}\cdot\text{L}^{-1}$). Tangshan (TS), Qinhuangdao (QH), Huludao (HL), Jinzhou (JZ), Panjin (PJ), Yingkou (YK), Dalian (DL) and Dandong (DD).

(downstream of the Dalin River), YK1 (midstream of the Daliao River), and DD1 (the Dayang River) $> 35 \text{ ng}\cdot\text{L}^{-1}$. The greatest concentration of $\sum\text{PFCs}$ was observed at JZ5 ($1.2 \times 10^2 \text{ ng}\cdot\text{L}^{-1}$, downstream of the Dalin River), followed by JZ4 ($76 \text{ ng}\cdot\text{L}^{-1}$, midstream of the Dalin River) and JZ3 ($76 \text{ ng}\cdot\text{L}^{-1}$, upstream of the Dalin River). In this case, relatively great concentrations of $\sum\text{PFCs}$ were observed in water samples along the entire Dalin River. It has been reported that 60% of untreated industrial wastewater and amounts of domestic sewage are discharged from cities flowing into the Dalin River [26,27]. Because concentrations of PFCs in rivers are associated with waste waters [28–30], and perfluorooctane surfactants in waste waters have been suggested to be the major sources of PFCs such as PFOS and PFOA pollution in the river [31,32], discharge of industrial wastewater and domestic sewage was the major source of PFCs in the Dalin River. JZ5 was near oil wells, and it was downstream of a paper plant which was 10 km away from the sea, thus the use of PFCs in oil wells and paper plants and its discharges were the most likely sources of the greatest concentrations of PFCs in this location.

The arithmetic mean concentrations (values less than the MDL were equal to half of the MDL) of PFOS ($2.5 \text{ ng}\cdot\text{L}^{-1}$) and PFOA ($8.9 \text{ ng}\cdot\text{L}^{-1}$) observed in surface waters of the coastal regions of the NBS, were less than those in surface waters in other Chinese cities. However, concentration of PFOS in surface water from Yingkou ($11 \text{ ng}\cdot\text{L}^{-1}$) was greater than those reported for other Chinese cities except Dongguan ($94 \text{ ng}\cdot\text{L}^{-1}$) [11,33,34]. Concentrations of PFOS in water samples from Dalian ($0.9 \text{ ng}\cdot\text{L}^{-1}$) were comparable with those collected from Dalian coastal waters [18]. The concentration of PFOA in Jinzhou ($56 \text{ ng}\cdot\text{L}^{-1}$) was greater than those reported for other Chinese cities except Shanghai ($152 \text{ ng}\cdot\text{L}^{-1}$) [11,33,34].

3.1.2. PFCs in sediments

Sediment has been suggested as a final sink for neutral organic pollutants [35]. However, there are few reports on PFCs in sediments. Concentrations of PFCs observed in sediments in this

Table 3. PFC concentrations ($\text{ng}\cdot\text{g}^{-1}$ dw) in sediments collected from the Bohai Sea, northern China.

ID	PFOS	PFOA	PFHxA	PFDA	PFUnA
DD3	<0.1	<0.1	<0.1	<0.1	0.2
TS1	<0.1	<0.1	<0.1	<0.1	0.1
TS4	<0.1	<0.1	<0.1	<0.1	0.3
TS5	<0.1	<0.1	<0.1	<0.1	0.2
TS6	<0.1	<0.1	<0.1	<0.1	0.2
TS7	<0.1	<0.1	<0.1	<0.1	0.2
HL1	<0.1	<0.1	<0.1	<0.1	0.4
HL2	<0.1	<0.1	<0.1	<0.1	0.2
HL3	<0.1	<0.1	<0.1	<0.1	0.2
HL4	<0.1	<0.1	0.3	<0.1	0.3
HL5	<0.1	<0.1	<0.1	<0.1	0.3
JZ4	<0.1	<0.1	<0.1	<0.1	0.2
JZ5	2.0	0.3	<0.1	0.3	0.2
PJ2	<0.1	0.2	<0.1	<0.1	0.2
QH1	<0.1	<0.1	<0.1	<0.1	0.3
QH2	1.5	0.5	0.2	1.0	<0.1
QH3	1.6	<0.1	0.4	<0.1	0.1
mean	0.2	0.1	0.1	0.1	0.1
SD	0.5	0.1	0.1	0.1	0.2
median	<0.1	<0.1	<0.1	<0.1	<0.1
geometric mean	<0.1	<0.1	<0.1	0.1	<0.1
geometric SD	2.7	1.7	1.6	1.8	2.1

Notes: Concentrations less than method detection limit (MDL) were assumed to be half the MDL for statistical purposes. PFOS, perfluorooctanesulfonate; PFOA, perfluorooctanoic acid; PFHxA, perfluorohexanoic acid; PFNA, perfluorononanoic acid; PFUnA, perfluoroundecanoic acid.

study were relatively small (Table 3), and results for samples for which all PFCs were less than the detection limit were not presented. PFOS was detected at locations JZ5 (midstream of the Dalin River), QH3 (branch water tidal flat) and QH2 (upstream of river tidal flat). Concentrations of PFOS at these three locations were greater, with concentrations of 2.0, 1.6 and 1.5 $\text{ng}\cdot\text{g}^{-1}$ dw, respectively. PFOA was detected only at locations JZ5 (midstream of the Dalin River), PJ2 (harbour from the open sea) and QH2 (upstream of river tidal flat). The greatest concentrations of PFOA were observed at location QH2 (0.5 $\text{ng}\cdot\text{g}^{-1}$ dw, upstream of river tidal flat), followed by JZ5 (0.3 $\text{ng}\cdot\text{g}^{-1}$ dw, midstream of the Dalin River) and PJ2 (0.2 $\text{ng}\cdot\text{g}^{-1}$ dw, harbour from the open sea). However, PFUnA was detected in sediments from approximately half of the locations ($n = 16$). Most of the PFCs were detected at location QH2, which was upstream of a tidal flat, and downstream of a dammed river with a partially opened flood gate. Concentrations of \sum PFCs in sediment ranged from ND to 4.3 $\text{ng}\cdot\text{g}^{-1}$ dw, with maximum concentrations of \sum PFCs observed at QH2 (4.3 $\text{ng}\cdot\text{g}^{-1}$ dw, upstream of the river tidal flat), followed by locations QH3 (2.3 $\text{ng}\cdot\text{g}^{-1}$ dw, branch water tidal flat) and PJ2 (1.1 $\text{ng}\cdot\text{g}^{-1}$ dw, harbour from the open sea). These three locations are all tidal flats, with relatively great salinities, and these locations were generally more urbanised and affected by activities such as fishing. The greatest concentrations of \sum PFCs in water were not found at these locations but were from the three Dalin River locations JZ5, JZ4 and JZ3.

Comparisons were made between concentrations of PFOS and PFOA in sediments of the coastal NBS and concentrations observed in other countries (Table 4). Concentrations of PFOS in sediments from the coastal NBS were comparable with those reported for San Francisco Bay area, USA [16]. However, they were greater than those reported for rivers in tidal flat areas of the Ariake Sea [35], rivers and lakes in Denmark [36], or the Roter Main River in Bayreuth, Germany [14]. Concentrations of PFOS in sediments from the coastal NBS were less than those reported for the Kyoto River, or the Osaka River in Japan [37]. Concentrations of PFOA in sediments from the coastal NBS were comparable to those of the San Francisco Bay area, but less than those in the Kyoto River [37], or Ariake Sea [35] in Japan.

Table 4. Comparison of perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) concentrations in sediment.

Location	Concentration (ng · g ⁻¹ dw)		Reference
	PFOS	PFOA	
Coastal regions of north Bohai Bay, China	<0.100–1.97	<0.100–0.542	This study
San Francisco Bay area, USA	ND–3.76	ND–0.625	[16]
Ariake sea, Japan	0.09–0.14	0.84–1.10	[35]
Danish Roter Main River, Bayreuth, Germany	<1.00	<0.40	[36]
Kyoto area River, Japan	<0.05–0.537	<0.025–0.175	[14]
Osaka River	<0.33–11	1.3–3.9	[37]
	<1.00–6.4	<0.100	[37]

Note: ND, not detected.

3.2. Correlations between concentrations of PFCs in water and sediment

There are two predominant opinions about the major sink of PFCs. One opinion is that the water column is a potential sink of PFCs in the environment [35]. Owing to their chemical–physical properties, most PFCs will stay in the aqueous phase rather than partitioning to solids, as do many neutral organic chemicals. If PFCs preferentially partition to the water column rather than to sediment, little accumulation in sediments would be expected. Alternatively, because PFCs are known to bind tightly to some proteins such as albumin [38], they could be deposited into sediments due to sedimentation of those specific proteins. Therefore, sediments are generally the primary ultimate sink for hydrophobic organic contaminants [15] and have been suggested to be important sinks for the ultimate fate and distribution of PFCs in the environment [39]. It has also been suggested that sediment could be a major source of perfluorinated surfactants (PFSs) to the food web of the Lake Ontario and that this could be mediated through accumulation of PFSs precursors in sediment [39]. The limited available data indicate that some PFCs such as PFOS strongly adsorb to solids, and that sewage sludge is widely suspected as a major sink of PFCs entering municipal waste streams [16].

To determine the primary medium in which PFCs will occur, one must conduct a mass balance calculation. In this study, concentrations were measured, but because the total masses of sediment and water were unknown, it was impossible to calculate the total mass of PFCs in each medium. However, because concentrations of PFCs in sediments were greater than those in water, sediments might be a useful integrating medium for monitoring. In general, \sum PFCs were more detectable in sediments than in waters of the coastal NBS (Figure 3). Similar results have also been observed in the Roter Main River, Bayreuth, Germany [14]. The sediment-to-water ratio ranged from ND to 3.4×10^3 , and most of the concentrations of \sum PFCs were 10- to 100-fold greater in sediment than in water. This indicates that sediments were a potential sink for PFCs, and that PFCs may sorb more strongly to solids than to the aqueous phase, and thus sediments can serve as an integrating monitor of long-term status and trends. However, owing to the lack of sediment samples that contained detectable PFOS and PFOA, further analysis of individual PFCs partitioning between sediment and water could not fully be addressed at this time.

3.3. Correlations between PFCs and TOC and other factors

No correlations were observed between concentrations of PFCs in sediment and any of the parameters such as TOC, TN and pH, a result that is consistent with the observations of a previous study

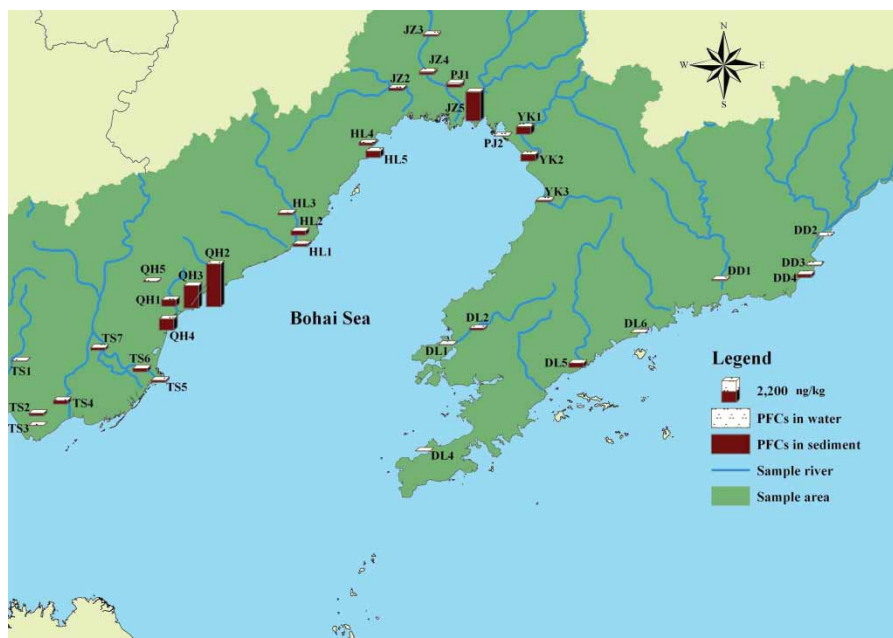


Figure 3. Comparison of \sum PFCs in water ($\text{ng}\cdot\text{kg}^{-1}$) and sediment samples ($\text{ng}\cdot\text{kg}^{-1}$ dw) among locations. Tangshan (TS), Qinhuangdao (QH), Huludao (HL), Jinzhou (JZ), Panjin (PJ), Yingkou (YK), Dalian (DL) and Dandong (DD).

[14]. The TOC content of sediments from coastal NBS ranged from 0.28 to 2.07%. The TN content of sediment samples ranged from 0.02 to 0.28%, and pH of sediment samples ranged between 5.07 and 8.29. There was, however, a weak negative correlation between concentrations of PFCs in water and water salinity.

4. Conclusions

Concentrations of PFCs in both sediments and water of the coastal NBS were relatively small in most samples, but greater concentrations of \sum PFCs were observed in water samples along the entire Dalin River, midstream portions of the Daliao and Dayang Rivers, and in sediments from upstream of river tidal flats and branch water tidal flats. The ratio of \sum PFCs in sediment and water indicated that sediments play a significant role as the ultimate PFC sink, especially for high molecular mass PFCs such as PFUnA. From the spatial distribution of PFCs, both sediment and water contained relatively great concentrations of PFCs in the lower reaches of rivers and tidal flat locations, and showed increasing concentrations approaching the bay, which may suggest possible point sources from the upper rivers or inland areas and sediment transportation or estuary deposition process. Because PFCs are still manufactured and used in China, further monitoring efforts should be made in terms of chemical characterisation and source identification due to greater concentrations of PFCs observed at some locations. The information reported here will provide the baseline against which future trends can be assessed.

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