



Technical Note

Perfluorinated compounds in Haihe River and Dagu Drainage Canal in Tianjin, China

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ABSTRACT

In this study, nine perfluorinated compounds (PFCs) were investigated in water and sediment of Haihe River (HR) and Dagu Drainage Canal (DDC), Tianjin, China. The total PFCs in water samples from DDC (40–174 ng L⁻¹) was much greater than those from HR (12–74 ng L⁻¹). PFC contamination was severe at lower reaches of HR due to industry activities, while high PFCs were found in the middle of DDC due to the effluents from wastewater treatment plants. Perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) were the predominant PFCs in aqueous phase. The total PFCs in sediments from DDC (1.6–7.7 ng g⁻¹ dry weight) were lower as compared to HR (7.1–16 ng g⁻¹), maybe due to the dredging of sediment in DDC conducted recently. PFOS was the major PFC in HR sediments followed by PFOA; while PFHxA was the major PFC in DDC sediments. Organic carbon calibrated sediment–water distribution coefficients (K_{oc}) were calculated for HR. The Log K_{oc} ranged from 3.3 to 4.4 for C7–C11 perfluorinated carboxylic acids, increasing by 0.1–0.6 log units with each additional CF₂ moiety. The log K_{oc} for 8:2 fluorotelomer unsaturated acid was reported for the first time with a mean value of 4.0. The log K_{oc} of PFOS was higher than perfluorooctanoic acid by 0.8 log units.

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1. Introduction

Perfluorinated compounds (PFCs) have been widely applied in commercial and industrial products for over 50 years because of their unique physical and chemical properties (Kissa, 2001; OECD, 2002). Due to the strong carbon–fluorine bonds, PFCs are persistent and have been found ubiquitously in the environment (Kannan et al., 2004; Higgins et al., 2005; Yamashita et al., 2005; Becker et al., 2008a; Oono et al., 2008; Ahrens et al., 2009a; Bao et al., 2009).

Aquatic environment is a primary phase for PFCs in the environment because of their polar nature. Significant concentrations of PFCs have been reported in aquatic environments around the world (Skutlarek et al., 2006; Senthilkumar et al., 2007; So et al., 2007; Nakayama et al., 2007; Naile et al., 2010). It is suggested that oceanic currents is a primary way for ionic PFCs transporting to Polar Regions, leading to their globally distribution (Armitage et al., 2006). Rivers are an important pathway for the transport of substances from lands to oceans. The PFC levels were detected in open ocean water with ranges of some tens to hundreds pg L⁻¹ (Yamashita et al., 2005; Ahrens et al., 2009a; Ahrens et al., 2010b), whereas PFC levels up to thousands of ng L⁻¹ were detected in inland rivers (Skutlarek et al., 2006; So et al., 2007). Compared to other places of the world, data on PFCs in aquatic environments of China is relatively scarce. PFCs have been detected in the Pearl River and

Yangtze River in China (So et al., 2007; Ju et al., 2008), with aqueous phase concentrations ranging from 0.99 to 99 ng L⁻¹ and <0.01 to 14 ng L⁻¹ for perfluorooctane sulfonate (PFOS); and 0.85 to 13 ng L⁻¹ and 2.0 to 260 ng L⁻¹ for perfluorooctanoic acid (PFOA), respectively.

Sediments in rivers sorb PFCs, acting as a sink for PFCs (Higgins and Luthy, 2006; Bao et al., 2010). Hence, the distribution between sediment and water in river is a key process to determine the fate of PFCs. However, the data on PFC distribution at sediment–water interface are relatively few (Higgins and Luthy, 2006; Becker et al., 2008b; Ahrens et al., 2009b, 2010a; Pan and You, 2010). The limited studies show that the distribution of different PFC homologues between sediment and water varied a lot. The short-chain perfluorinated carboxylic acids (PFCAs) (≤C8) were exclusively detected in the dissolved phase, whereas those long-chain PFCAs (>C8) and perfluoroalkyls sulfonates (PFASs) appeared to be bound to sediment (Ahrens et al., 2009b, 2010a). Furthermore, the sediment–water distribution of PFCs depends on water chemistry and sediment properties, such as pH (Higgins and Luthy, 2006; Ahrens et al., 2009b), organic carbon fraction of the sediment (f_{oc}) (Liu and Lee, 2005; Ahrens et al., 2009b), and salinity (Pan and You, 2010; You et al., 2010). Therefore, systematic field-based studies on sediment–water distribution of PFCs along entire river are pertinent to understand the fate of PFCs.

Tianjin is one of the four municipalities directly under the National Central Government and important commercial and industrial center in China with an area about 11 200 km² and a population

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of 11 million. The Haihe River (HR) is the largest water system in Huabei Region of China, flowing through Tianjin city to Bohai Bay. The Dagu Drainage Canal (DDC) is a primary drainage canal in Tianjin, receiving effluents from four main municipal wastewater treatment plants (WWTPs) and wastewaters from small factories and agriculture along its way to Bohai Bay. (Fig. 1; Tianjin Environment Protection Bureau, 2001).

The present study aimed to (1) demonstrate the spatial distribution of PFCs in water and sediment of HR and DDC in Tianjin; (2) evaluate the field-based sediment–water distribution of PFCs.

2. Materials and methods

2.1. Chemicals and reagents

Perfluorododecanoic acid (PFDoA, 95%) and PFOS (99%) were purchased from Sigma–Aldrich Chemical (St Louis, MO, USA). Perfluorohexanoic acid (PFHxA, >98%), perfluoroheptanoic acid (PFHpA, >98%), and perfluoroundecanoic acid (PFUnA, >96%) were purchased from Matrix Scientific (Columbia, SC, USA). PFOA (>98%) was obtained from Strem Chemicals (Bischheim, France). Perfluorononanoic acid (PFNA, >98%) and Perfluorodecanoic acid (PFDA, >98%) were purchased from Fluorochem (Derbyshire, UK). $^{13}\text{C}_8$ -Labeled PFOA ($^{13}\text{C}_8$ -PFOA) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). 8:2 fluorotelomer unsaturated acid (8:2 FTUCA), $^{13}\text{C}_2$ -8:2FTUCA and $^{13}\text{C}_4$ -Labeled sodium PFOS ($^{13}\text{C}_4$ -PFOS) were purchased from Wellington Laboratories (Guelph, Ontario, Canada). All the standards were obtained in methanol at concentrations of several $\mu\text{g mL}^{-1}$.

Waters Oasis WAX (6 cc) cartridges, used for solid phase extraction were from Waters Corporation. Ammonia hydroxide (25%), ammonium acetate (97%), sodium acetate (98.5%) and acetic acid (99.9%) were of analytical grade, and purchased from Guangfu Fine Chemical Research Institute, Tianjin, China. Methanol (HPLC grade)

from Dikma Technologies (Lake Forest, CA, USA) and Milli-Q water were used throughout the study.

2.2. Sampling campaign

Sixteen sites along HR (H1–H16) and eight sites along DDC (D1–D8) were sampled during April and May, 2010, respectively. The site locations are shown in Fig. 1, and their geographic information is given in Supplemented Material (SM), Table SM-1.

Two parallel water samples were collected at a depth of approximately 0.5 m below the surface with a stainless steel bucket, and stored in polypropylene (PP) bottles. Surface sediment samples (0–10 cm) were collected with a stainless steel grab sampler and placed in PP bags. The sediment samples were transported to laboratory at 0 °C, and then dried in a freeze-drier. All sampling vessels were cleaned using methanol, Milli-Q water, and water from the specific site before sampling. The HR and DDC are not wide, and hence only one sampling site was chosen along the midline at each section. Three travel blanks for water sample were checked for sampling events, PP bottles containing 500 mL Milli-Q water were shipped to the field and exposed to the same conditions as the real water sample. All samples were stored at –20 °C before extraction. All Teflon-containing laboratory materials were avoided during the experimental and sampling procedures to prevent possible contamination of PFCs.

Temperature of the water sample was in the range of 15–18 °C. The pH of water samples was determined and the values are listed in Table SM-1. The pH of water samples from HR did not vary a lot, ranging from 7.8 (H16) to 8.5 (H1, H9, and H10), while changed a bit for DDC, from 6.4 (D3 and D4) to 8.1 (D6 and D8). f_{oc} of sediments were determined by the method of potassium dichromate–sulfuric acid oxidation (Institute of Soil Science, Chinese Academy of Sciences, 1978), and are listed in Table SM-1. The f_{oc} of sediments from both HR and DDC varied greatly, from 2.1% (H13) to 11% (H1) for HR, and from 1.2% (D7) to 8.4% (D1) for DDC.

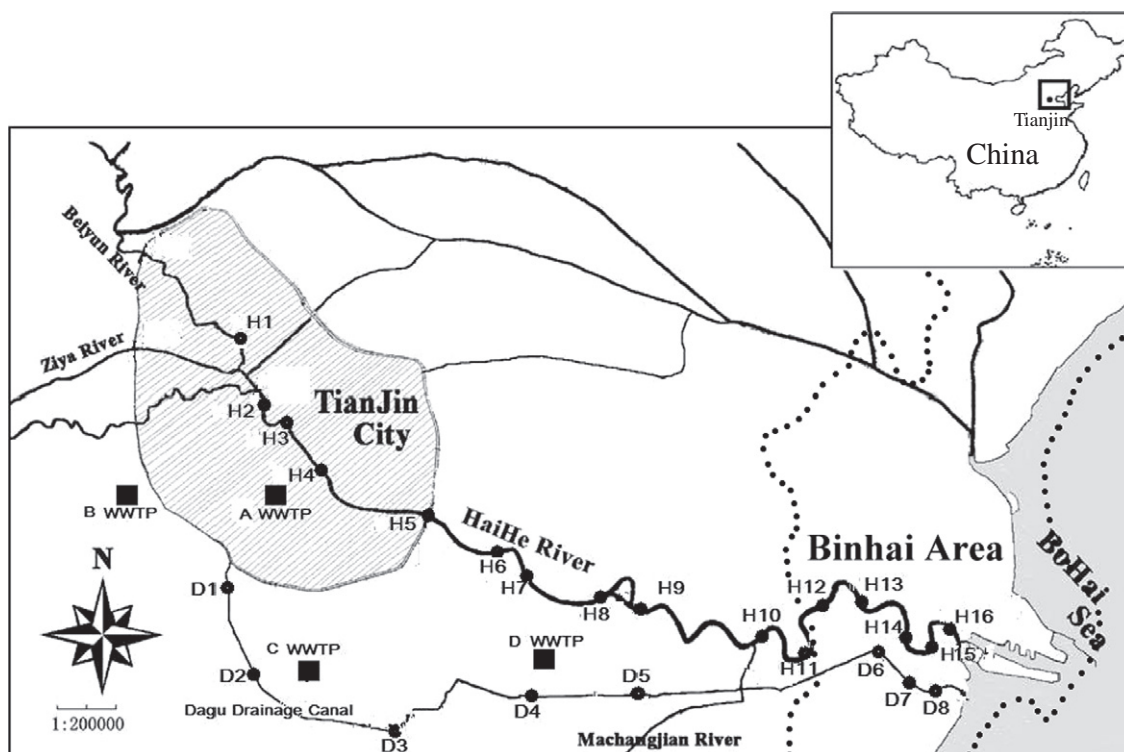


Fig. 1. Map of the sampling locations in Haihe River and Dagu Drainage River, Tianjin, China.

2.3. Extraction and analysis

Water sample extraction procedure used here was described elsewhere (Sun et al., 2009), which was modified according to Taniyasu et al. (2005). Briefly, the water samples were extracted using Oasis WAX extraction cartridges (150 mg/6 cc). Prior to loading of water samples, the WAX cartridges were preconditioned by passing 4 mL of 0.1% NH₄OH in methanol, followed by 4 mL of milli-Q water with gravity drop. A total of 500 mL water sample was filtered with a 1 µm glass fiber filter (Advantec, Toyo Roshi Kaisha, Japan) and then spiked with internal standards (including 5 ng of ¹³C-PFOA, 5 ng of ¹³C-PFOS and 5 ng of ¹³C 8:2 FTUCA). The sample was loaded on the preconditioned cartridge at a rate of 3 mL min⁻¹. The cartridges were then washed with 4 mL of 25 mM sodium acetate buffer (pH 4). Then, the target fraction was eluted with 4 mL of 0.1% NH₄OH in methanol with gravity drop. Finally, the extracted solutions were concentrated under gentle nitrogen stream to a volume of 0.5 mL.

The sediment samples were extracted using the method described previously (Sun et al., 2009). Briefly, 0.5 g dried sediment was weighted into 15 mL PP tube, and spiked with 5 ng of internal standards after wetted by 0.5 mL Milli-Q water. The spiked sediment was extracted three times with 2.5, 1.5, and 1.0 mL of methanol. Each extraction was performed by shaking the slurry for 10 min, sonicating for 20 min at 40 °C and centrifuging at 3500 rpm for 8 min. Then the combined extracts were cleaned up by adding 150 mg of Envicarb particles and shaking gently for 15 min. The solution was separated from Envicarb particles by centrifuging at 3500 rpm for 10 min, and concentrated under gentle nitrogen stream to a final volume of 0.5 mL.

Before analysis, the extract was filtered through a 0.2 µm nylon filter, and transferred to a 2 mL HPLC autosampler vial.

The extracts were analyzed on an Alliance 2695 Separations Module equipped with a Quattro Micro™ atmospheric pressure ionization tandem quadrupole mass spectrometer (MS1 quadrupole-MS2 quadrupole; Waters, USA). The MS-MS was operated in electrospray negative ionization. A 20 µL aliquot of the extract was injected into an X-Terra MS C₁₈ column (2.1 mm id. × 150 mm, 5 µm, Waters, Ireland) with 2.5 mM ammonium acetate methanol (A)/2.5 mM ammonium acetate water (B) as the mobile phases. The gradient elution was started at 10% A, increased to 60% A at 0.8 min, and then continuously increased to 100% at 12.8 min before reverting to original conditions at 14.3 min. The mobile phase flew at a rate of 250 µL min⁻¹, and column temperature was maintained at 40 °C. The desolvation gas flow rate and temperature were maintained at 600 L h⁻¹ and 300 °C, respectively. The collision energies for PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA and 8:2 FTUCA were 11, 11, 11, 13, 13, 12, 13, 45 and 15 eV, respectively, and the cone voltages were 12, 13, 14, 14, 16, 18, 18, 55 and 15 V, respectively.

Analyte quantitation was performed using internal calibration with ¹³C-PFOA, ¹³C-PFOS and ¹³C-8:2 FTUCA as internal standards. Seven point calibrations were prepared in methanol with concentration range from 0.1 to 100 µg L⁻¹. Linear 1/X weighted regressions, not forced through the origin, were based on surrogate standard calibration and have the correlation coefficient of greater than 0.99.

2.4. Quality assurance and quality control

Blanks were run every 7–8 samples to check for carryover and background contamination. All blanks were found to be below the limit of detection (LOD), where the LOD was defined as the concentration that yielded a signal-to-noise (S/N) ratio of equal to or higher than 3. Procedural blanks (500 mL of Milli-Q water for water sample and 0.5 g quartz sand for sediment, *n* = 5), were extracted in the same manner as the samples. Only PFOA (<0.08–0.12 ng L⁻¹)

were detected in water blanks and sediment blanks, but all below the limit of quantification (LOQ). The LOQ was defined as the concentration that yielded an S/N ratio of 10 or the lowest point at calibration curve calculated to be with 30% of its actual value, and ranged between 0.13 and 0.46 ng L⁻¹ for water sample and between 0.13 and 0.46 ng g⁻¹ for sediment sample (Table SM-2). Travel blank did not show extra PFC contamination as compared to procedure blank. Concentrations greater than or equal to LOD but less than LOQ were assigned a concentration twice that of the LOD, and those at or below the LOD were assigned a value of zero.

Matrix spike recoveries were determined by spiking 5 ng of each PFC standard into 500 mL water samples (*n* = 3) and 0.5 g sediment samples (*n* = 3) collected from site H5. The matrix spike recoveries for all analytes ranged between 82% and 105% for water sample, with the maximum standard deviation (SD) of 4.5%, and between 78% and 128% for sediment sample, with the maximum SD of 5.3% (Table SM-2). Duplicate samples were analyzed separately; their relative standard deviations were less than 12%.

3. Results and discussion

3.1. Spatial distribution of PFCs in water from Haihe River

The total concentration of the nine PFCs in water samples from HR ranged between 12 and 74 ng L⁻¹ (Fig. 2a), and relatively higher levels occurred in lower reaches (H9–H16) as compared to upper reaches (H1–H8). For the individual homologues, all PFCs except PFDoA were detected in water samples, and PFOA and PFHxA were the most prevalent PFCs, ranging between 4.4 and 42 ng L⁻¹ (with a mean value of 15 ng L⁻¹), and between 2.2 and 42 ng L⁻¹ (mean = 15 ng L⁻¹), respectively. These occupied 20–68% and 15–65% of the total PFCs (Fig. SM-1a), respectively. Similar to the total PFCs, the concentration of PFOA and PFHxA was higher in lower reaches, indicating some extra sources along the lower reaches. The lower reaches of HR are located in Tanggu District, an historic industrial district belonging to Binhai Area (Fig. 1), which is recognized as the third economic center in China besides Shanghai and Guangzhou. The industry may act as point sources and non-point sources through surface runoff for the PFCs in HR.

The long-chain PFCAs were measured with less frequency and at lower concentrations, and PFDoA was even not detected in water phase. As a main metabolite of 8:2 FTOH (Liu et al., 2007; Wang et al., 2009), 8:2 FTUCA was detected in most of the water samples (14 out of 16) from HR, however, its level was low, ranging from <LOD to 0.75 ng L⁻¹ (Fig. 2a). The 8:2 FTUCA was proposed to further degraded to PFOA and other products, and hence the coexistence of 8:2 FTUCA and PFOA in HR seems to indicate that PFOA may not only come from the direct discharge, but also from the degradation of precursor compounds, such as 8:2 FTOH.

Though PFOS was detected in all water samples from HR, its concentration is relatively low as compared to PFOA and PFHxA with a mean value of 3.7 ng L⁻¹ (Fig. 2a). These values contributed only 4–29% of the total PFCs (Fig. SM-1a). The ratio of PFOA/PFOS in HR is higher as compared to the rivers from south China (So et al., 2004; So et al., 2007). No significant variation in the level of PFOS in water samples was found between the upper and lower reaches.

The levels of PFOA and PFOS in HR measured in this study were compared with those in other aquatic environments around the world (Table SM-3). Aqueous concentrations of PFOA in HR were at relatively higher levels except for Yangtze River, Shanghai China (So et al., 2007). The aqueous PFOS concentrations in HR were relatively low than those reported from Yangtze River Estuary (Pan and You, 2010), Zhujiang River, Guangdong (So et al., 2007) in China, and rivers from Japan (Senthilkumar et al., 2007), but were comparable to those observed in Yangtze River, Shanghai (So et al., 2007).

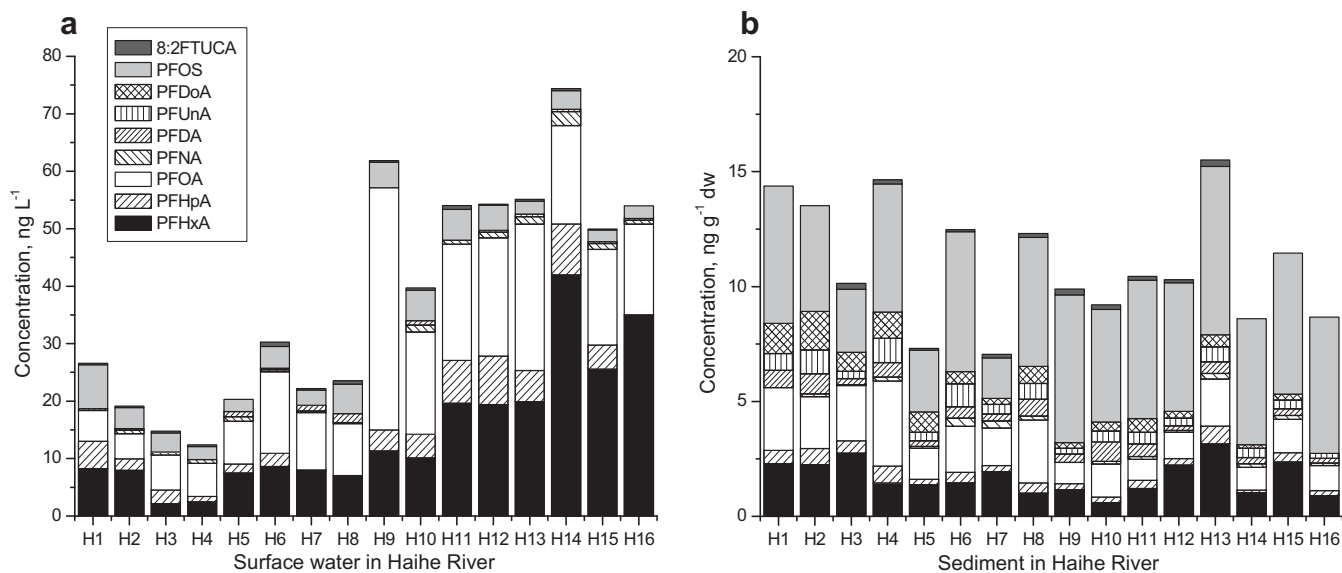


Fig. 2. Spatial distributions of PFCs in surface water (a) and sediment (b) from Haihe River.

As for PFHxA, high concentration (47 ng L^{-1}) was found in Asan reservoir in Korea, accompanied by high levels of PFOA (50 ng L^{-1}) and PFOS (450 ng L^{-1}) (Naile et al., 2010). Up to 3040 ng L^{-1} of PFHxA were detected in Moehne River and its tributaries near Brilon-Scharfeberg, Europe, accompanied by similar levels of other PFCs (Skutlarek et al., 2006). That was attributed to non-point sources of agricultural contamination and effluents of WWTPs. Further study is still needed to find specific sources for PFHxA in HR.

3.2. Spatial distribution of PFCs in sediment from Haihe River

The total concentration of PFCs in the sediment of HR ranged between 7.1 and 16 ng g^{-1} dry weight (Fig. 2b), and no uniform spatial distribution tendency was found. All the 9 PFCs except for PFNA and 8:2 FTUCA were detected in all sediment samples. PFOS was the predominant PFC, ranging between 1.8 and 7.3 ng g^{-1} (with a mean value of 5.2 ng g^{-1}), followed by PFOA, (0.9 – 3.7 ng g^{-1} with a mean of 1.80 ng g^{-1}) and PFHxA (0.6 – 3.2 ng g^{-1} with a mean of 1.7 ng g^{-1}). Although the long-chain PFCAs were still at low levels, but the detection frequency and concentrations increased with the carbon chain. The 8:2 FTUCA was detected in most sediment samples (11 out of 16), ranging between $<\text{LOD}$ and 0.3 ng g^{-1} (Fig. 2b). The percentage contributions of PFOS, PFOA and PFHxA to the total PFCs were 27–68%, 9–25%, and 6–28%, respectively (Fig. SM-1b).

As shown in Table SM-3, PFOS concentrations in sediments from HR were 1–2 orders of magnitude lower than those in Yangtze River Estuary, China (Pan and You, 2010), but higher than other areas of China, such as Zhujiang River in Guangzhou (Bao et al., 2010), Daliao River in Liaoning Province and Huangpu River in Shanghai (Bao et al. 2009; Bao et al. 2010). From a worldwide view, the sedimentary PFOS levels in HR were higher than those in rivers of Japan (Senthilkumar et al., 2007). The levels of PFOA in HR sediments were one order of magnitude higher than those reported for other areas of China that listed in Table SM-3 and comparable to those found in rivers of Japan (Senthilkumar et al., 2007).

Overall, different composite profiles were observed between water and sediment, indicating that the distribution of individual PFCs between water and sediment depends on their physicochemical characteristics (Fig. SM-1). Short-chain PFCAs tend to exist in water phase, while long-chain PFCAs, PFOS and 8:2 FTUCA seem to bind more strongly to sediment. The distribution of PFCs between water and sediment will be discussed in detail in Section 3.4.

3.3. Spatial distribution of PFCs in water and sediment from Dagu Drainage Canal

The total PFCs in water samples from DDC was in the range between 40 and 174 ng L^{-1} , much greater than those in HR (Fig. 3a). Similar to those in HR, PFHxA and PFOA were the prevalent PFCAs, with their aqueous phase concentrations being 14 – 124 ng L^{-1} (mean of 47 ng L^{-1}) and 14 – 65 ng L^{-1} (mean of 32 ng L^{-1}), respectively, and their percentage contributions to the total PFCs being 15–80 and 15–41% (Fig. SM-2a). PFOS was also detected at relatively high levels in water samples from DDC, ranging from 1.2 to 73 ng L^{-1} (mean of 22 ng L^{-1}), which contributes 1–46% to the total PFCs. The PFOS concentration is much greater as compared to HR.

Relatively higher concentrations of PFCs were detected in the middle reaches of the DDC. PFOA and PFOS were high at D3–D5, while PFHxA was high at D5–D8, indicating different sources of PFC homologues. The DDC is a main sewage drainage canal for Tianjin, and several WWTPs discharge their effluents into DDC (Fig. 1). Our unpublished data on six municipal WWTPs in Tianjin showed that PFOA was the dominant PFC with concentrations ranging from 80 to 145 ng L^{-1} , followed by PFOS (2.6 and 98 ng L^{-1}). The effluent from municipal WWTPs may lead to the increased levels of PFOA and PFOS in the middle reaches of DDC. The reason for the high level of PFHxA found in the lower reaches of DDC may due to point industrial source and need further investigation. A sharp decrease in total PFC level was observed at D8, and this may be due to the dilution by inwelling seawater.

The levels of PFCs in sediment samples from DDC were very low, with the total PFCs ranging between 1.6 and 7.7 ng g^{-1} (Fig. 3b). The unexpected low levels of PFCs in DDC sediments as compared to HR could be ascribed to a recent dredging in DDC. The spatial PFC concentration in DDC sediments is similar to that of water phase, indicating that PFCs could be quickly adsorbed onto the sediment. PFHxA was the major PFC in DDC sediment, ranging between 0.13 and 3.5 ng g^{-1} with a mean of 1.5 ng g^{-1} . The contribution of PFHxA to total PFCs ranged from 6% to 68% (Fig. SM-2b). Similar to the tendency in water phase, PFHxA in the sediments of DDC was greater in lower reaches. This strongly indicates that there are specific point sources for PFHxA in the area along the lower reaches of DDC. The levels of PFOA and PFOS ranged between 0.27 and 1.7 ng g^{-1} (mean of 0.89 ng g^{-1}) and from 0.09 to 2.3 ng g^{-1} (mean of 0.67 ng g^{-1}), respectively. Their contributions to the total PFCs in the sediment were 10–32% for PFOA

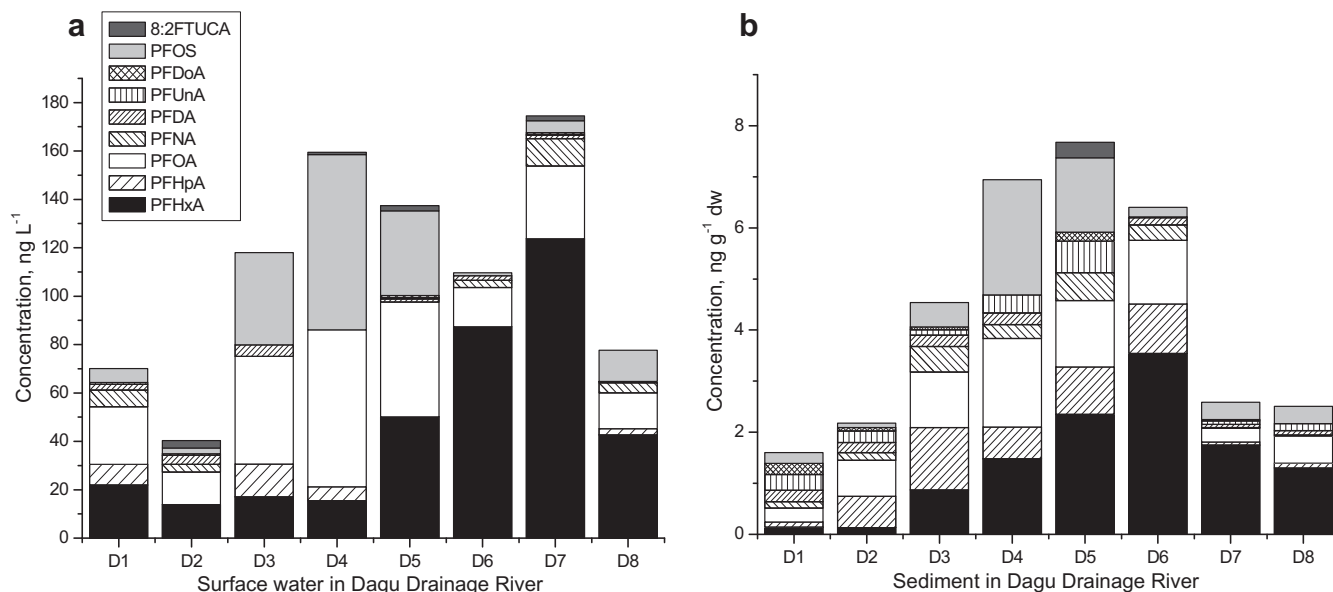


Fig. 3. Spatial distributions of PFCs in surface water (a) and sediment (b) from Dagu Drainage Canal.

and 3–33% for PFOS (Fig. SM-2b). Other PFCs were at very low levels, and 8:2 FTUCA was only detected in one sediment collected from D5 (0.30 ng g^{-1}) (Fig. 3b).

3.4. Distribution coefficient of PFCs between sediment and water in Haihe River

Distribution coefficient between sediment and water (K_D) from HR were calculated according to Eq. (1) (Table SM-4), and their ranges are listed in Table 1.

$$K_D = C_{\text{sediment}}/C_{\text{water}} \quad (1)$$

where C_{sediment} is PFC concentration in the sediment (ng kg^{-1}) and C_{water} is PFC concentration in water (ng L^{-1}). Previous studies showed that the sorption of individual PFCs, such as PFOS, PFDA (Higgins and Luthy, 2006), n-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA) (Higgins and Luthy, 2006; Ahrens et al., 2009b) and 8:2 FTOH (Liu and Lee, 2005) on sediment depends primarily on f_{oc} of the sediment. Hence, f_{oc} normalized distribution coefficient (K_{oc}) was calculated according to Eq. (2) in order to give a comparison.

$$K_{\text{oc}} = K_D \times 100/f_{\text{oc}} \quad (2)$$

Correlation between K_D and f_{oc} (Table SM-1) were made for different PFC homologues (Table 1), and no significant correlation was found ($p > 0.05$). This is different to the laboratory research of

Table 1
Average $\log K_D^a$ and $\log K_{\text{oc}}^a$ at sediment–water interface from Haihe River.

Compound	Sampling locations	$\log K_D$	$\log K_{\text{oc}}$	Correlation between $\log K_D$ and f_{oc} (i^2) ^c
PFHxA	H1–H8	2.5 ± 0.3 (2.2–3.1; $n = 8$)	3.7 ± 0.4 (3.3–4.7; $n = 8$)	0.28 ($p > 0.05$)
	H9–H16	1.8 ± 0.3 (1.4–2.2; $n = 8$)	3.1 ± 0.2 (2.7–3.4; $n = 8$)	
	H1–H16	2.2 ± 0.4 (1.4–3.1; $n = 16$)	3.4 ± 0.4 (2.7–4.7; $n = 16$)	
PFHpA	H1–H8	2.4 ± 0.3 (2.1–2.9; $n = 6$)	3.6 ± 0.4 (3.0–4.0; $n = 6$)	0.25 ($p > 0.05$)
	H9–H16	1.7 ± 0.3 (1.1–2.2; $n = 7$)	3.0 ± 0.3 (2.4–3.3; $n = 7$)	
	H1–H16	2.0 ± 0.5 (1.1–2.9; $n = 13$)	3.3 ± 0.5 (2.4–4.0; $n = 13$)	
PFOA	H1–H8	2.5 ± 0.3 (2.2–2.8; $n = 8$)	3.7 ± 0.3 (3.2–4.2; $n = 8$)	0.18 ($p > 0.05$)
	H9–H16	1.8 ± 0.2 (1.3–1.9; $n = 8$)	3.1 ± 0.3 (2.6–3.5; $n = 8$)	
	H1–H16	2.1 ± 0.4 (1.3–2.8; $n = 16$)	3.4 ± 0.4 (2.6–4.2; $n = 16$)	
PFNA	H1–H8	2.5 ± 0.5 (1.8–3.0; $n = 7$)	3.8 ± 0.4 (3.3–4.3; $n = 7$)	0.42 ($p > 0.05$)
	H9–H16	2.1 ± 0.2 (1.8–2.3; $n = 7$)	3.4 ± 0.3 (3.1–3.9; $n = 7$)	
	H1–H16	2.3 ± 0.4 (1.8–3.0; $n = 14$)	3.6 ± 0.4 (3.1–4.3; $n = 14$)	
PFDA	H1–H8	3.0 ± 0.5 (2.4–3.5; $n = 6$)	4.2 ± 0.3 (3.8–4.7; $n = 6$)	0.63 ($p > 0.05$)
	H9–H16	NA ^b ($n = 2$)	NA ($n = 2$)	
	H1–H16	2.9 ± 0.4 (2.4–3.5; $n = 8$)	4.2 ± 0.3 (4.0–4.5; $n = 8$)	
PFUnA	H1–H8	NA ($n = 0$)	NA ($n = 0$)	0.70 ($p > 0.05$)
	H9–H16	3.1 ($n = 5$)	4.4 ± 0.3 (4.0–4.8; $n = 5$)	
	H1–H16	3.1 ($n = 5$)	4.4 ± 0.3 (4.0–4.8; $n = 5$)	
PFOS	H1–H8	3.1 ± 0.2 (2.8–3.4; $n = 8$)	4.3 ± 0.2 (3.8–4.6; $n = 8$)	0.17 ($p > 0.05$)
	H9–H16	3.2 ± 0.2 (3.0–3.5; $n = 8$)	4.6 ± 0.3 (4.2–5.1; $n = 8$)	
	H1–H16	3.2 ± 0.2 (2.8–3.5; $n = 16$)	4.4 ± 0.3 (3.8–5.1; $n = 16$)	
8:2 FTUCA	H1–H8	2.6 ± 0.4 (2.1–3.0; $n = 5$)	3.9 ± 0.5 (3.1–4.5; $n = 5$)	-0.22 ($p > 0.05$)
	H9–H16	2.8 ± 0.2 (2.8–3.0; $n = 6$)	4.1 ± 0.3 (3.1–4.5; $n = 6$)	
	H1–H16	2.7 ± 0.3 (2.1–3.0; $n = 11$)	4.0 ± 0.4 (3.6–4.5; $n = 11$)	

^a K_D and K_{oc} in liters per kilogram.

^b NA = not available.

^c Spearman's correlation, p value < 0.05 ; analyzed by the statistical software package SPSS 16.0 (SPSS, 2008).

Higgins and Luthy (2006) and field findings from Tokyo Bay (Ahrens et al., 2009b), in which strong correlation between K_D and f_{oc} was found, but in accordance with the field research from the Netherlands (Kwadijk et al., 2010). The special physical and chemical properties of anionic PFCs make both hydrophobic and electrostatic effects co-influence their sorption (Higgins and Luthy, 2006). Besides sediment property, water chemistry may also influence the sorption of PFCs on sediment. A significant correlation was found between pH and sedimentary concentrations of some PFCs (Higgins and Luthy, 2006; Ahrens et al., 2009b; You et al., 2010). It has also been proved that Ca^{2+} and salinity enhance PFC sorption onto sediment (Higgins and Luthy, 2006; Pan et al., 2009; You et al., 2010).

The HR investigated in this study is not too long (70 km), however, its aquatic chemistry changes greatly. The HR is divided into two parts by a gate at H8, the upper reach (H1–H8) was fresh water area, whereas the lower reach (H9–H16) was salty water area (Yu et al., 2009). Hence, the ranges and mean values of K_D and K_{OC} are separately presented for the upper and lower reaches of HR (Table 1). Higher K_D and K_{OC} were found for PFOS and 8:2 FTUCA in lower reaches than those in upper reaches, which is accordance with the above discussion that salinity enhance PFC sorption (Higgins and Luthy, 2006; Pan et al., 2009; You et al., 2010). However, opposite trend was found for short-chain PFCAs and PFNA; higher hydrophilicity of these compounds and other complex aquatic chemistry in this area might be responsible for these results. Moreover, at some sites, the distribution between water and sediment may have not reached equilibrium if an adjacent discharge exists. Hence, in large-scale and complex field studies, like the Netherlands (Kwadijk et al., 2010) and Haihe River, both the sediment characteristics and aquatic chemistry may influence PFC partition between water and sediment.

The average $\log K_D$ of 3.1 ± 0.2 ($n = 16$) for PFOS in this study is much higher than the field $\log K_D$ (1.2 – 1.6; 2.1 ± 0.1 ; 2.53 ± 0.35) in literatures (Becker et al., 2008b; Ahrens et al., 2010a; Kwadijk et al., 2010). For PFOA, the average value of $\log K_D$ (2.1 ± 0.4) is also higher than previous reports, i.e. 0.04 ± 0.03 (Ahrens et al., 2010a), 0.18 – 0.48 (Becker et al., 2008b) and 1.83 ± 0.40 (Kwadijk et al., 2010). This may be due to differences in sediment characteristics between different studies, but differences in the state of sediment–water equilibrium may also explain part of the variation.

Among the different PFC homologues, the average $\log K_{OC}$ generally increased with the carbon chain of PFCAs. Exception occurred between PFHxA and PFHpA, where a slight reduction in $\log K_{OC}$ was found. Earlier laboratory study of Higgins and Luthy (2006) and a recent field study at Tokyo Bay (Ahrens et al., 2009b) both showed a sustain increase in $\log K_{OC}$ with the increasing carbon length. However, increasing $\log K_{OC}$ with carbon chain of PFCAs was only observed from PFOA to PFNA in aquatic environment in the Netherlands, whereas no increase was observed from PFNA to PFDoA (Kwadijk et al., 2010). In this study, the average $\log K_{OC}$ for PFCAs ranged from 3.3 for PFHpA to 4.4 L kg^{-1} for PFUNA, increasing by 0.1–0.6 log units with each CF_2 moiety. The $\log K_{OC}$ for 8:2 FTUCA was reported for the first time with relatively high value of 4.0 ± 0.4 (mean), indicating its strong adsorption on sediment. However the value of $\log K_{OC}$ for 8:2 FTUCA was less than that of PFDA (mean = 4.2 ± 0.3), which has the same carbon chain with 8:2 FTUCA. This may be due to the substitution of fluorine atom by hydrogen, which is expected to reduce the lipophilicity of the molecule, leading to a smaller $\log K_{OC}$ for 8:2 FTUCA. Furthermore, the double bond in 8:2 FTUCA should also enhance the hydrophilicity of 8:2 FTUCA. The average $\log K_{OC}$ of PFOS was higher than the corresponding carboxylic acids (PFNA) by 0.8 log units, and this is in consistent with previous reports (Higgins and Luthy, 2006; Ahrens et al., 2010a).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.03.060.

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