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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 CF_2 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 perfluoronanoic acid by 0.8 log units.

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 km^2 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 DDR 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). $^{13}C_8$-Labeled PFOA ($^{13}C_8$-PFOA) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). 8:2 fluorotelomer unsaturated acid (8:2 FTUCA), $^{13}C_2$-8:2FTUCA and $^{13}C_4$-Labeled sodium PFOS ($^{13}C_4$-PFOS) were purchased from Wellington Laboratories (Guelph, Ontario, Canada). All the standards were obtained in methanol at concentrations of several $\mu g\ mL^{-1}$.

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.

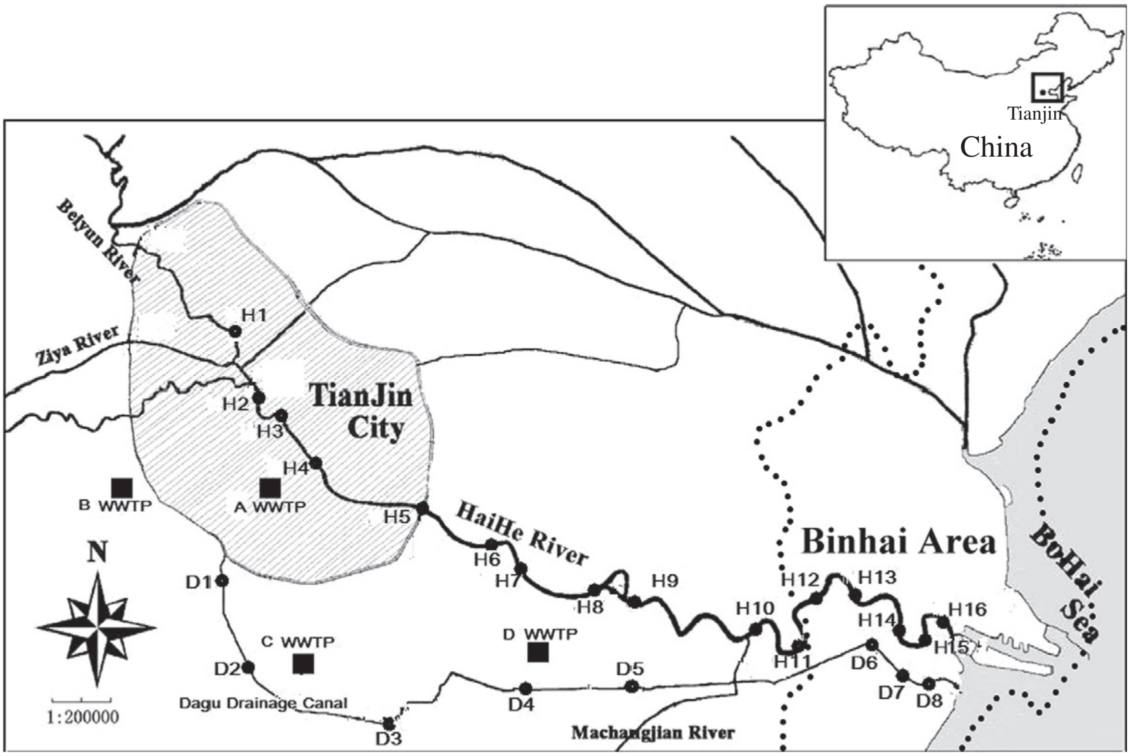

Fig. 1. Map of the sampling locations in Haihe River and Dagu Drainage River, Tianjin, China.