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# Spatial and vertical variations of perfluoroalkyl substances in sediments of the Haihe River, China

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## ARTICLE INFO

### Article history:

Received 21 October 2013

Revised 2 December 2013

Accepted 10 December 2013

Available online 5 July 2014

### Keywords:

Perfluoroalkyl substances (PFASs)

Sediment core

Sediment quality

Haihe River

## ABSTRACT

The levels of six perfluoroalkyl substances (PFASs) in surface sediment and their vertical variations in dated sediment cores from the Haihe River were investigated; studied substances included perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctane sulfonate (PFOS), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), and perfluorododecanoic acid (PFDoA). Results showed that the total PFAS concentration in surface sediment ranged between 0.52 and 16.33 ng/g dry weight (dw) with an average of 3.47 ng/g dw, with PFOS and PFOA as the dominant PFASs. In general, the PFAS concentrations in the mainstream increased from the upper to the lower reaches, except that a drop occurred downstream of the Erdao dam. Although the PFASs in the sediment cores did not show a clear decreasing or increasing trend with depth, the three cores had a similar vertical variation. The PFAS levels were relatively low in the surface sediment, and reached the first high point at 8–20 cm as a result of the wide use of PFASs from 1990 to 2000. After that the PFAS levels decreased, and then increased to a second high point at about 40–48 cm, which might be caused by the leaching of PFASs in sediment. Because PFASs have hydrophilic groups and relatively high solubility, the PFASs will transfer from the upper to lower layers of sediment when water infiltration occurs, leading to the fluctuation of PFAS levels in sediment cores. This study suggests that both the temporal variation of sources and transfer processes of PFASs in sediments are important factors influencing the vertical variation of PFASs in sediment cores.

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## Introduction

Perfluoroalkyl substances (PFASs) are a class of perfluorinated chemicals that consist of a perfluoroalkyl chain and a terminal sulfonate or carboxylate group. PFASs have been manufactured and widely used in various industries since the 1950s due to their ability to repel water and oil, resistance to heat, and chemical inertness (Buck et al., 2011; Paul et al., 2009; Kubwabo et al., 2004), thus it can be expected that large amounts of PFASs have been released into the environment. Due to their properties of high persistence, bioaccumulation, toxicity, and potential carcinogenicity, PFASs have become one of the emerging contaminants

in the field of environment sciences. Perfluorooctane sulfonate (PFOS) and its salts, in particular, were listed in Annex B of Persistent Organic Pollutants by the Stockholm Convention in May 2009. Recent studies indicated that PFASs can accumulate in sediment via sorption (Chen et al., 2011; Xia et al., 2012), and sediment may be an important source and sink of PFASs. Thus the studies on PFAS levels in sediments are of great importance. In addition, vertical variations of PFAS concentrations in sediments with depth might be able to illustrate temporal trends in sediment PFAS contamination.

So far, some studies have reported the distribution of PFASs in top sediments from different water bodies (Möllera et al., 2010;

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Labadie and Chevreuil, 2011; Zhang et al., 2012b). Several works have reported vertical variations of PFAS levels in sediment cores (Bao et al., 2010; Ahrens et al., 2009; Stock et al., 2007), but few of these works have studied sediment cores deeper than 10 cm. For example, Ahrens et al. (2009) studied the perfluoroalkyl carboxylic acid and perfluoroalkyl sulfonate levels in sediment cores from Tokyo bay in Japan and found that the vertical variation of PFASs showed no clear increasing or decreasing trend with depth, and perfluorooctane sulfonamide seemed to bind more strongly to sediment than perfluoroalkyl carboxylic acids. Bao et al. (2010) reported an overall decreasing trend of perfluoroalkyl carboxylic acids with depth in sediment cores from the Zhujiang River and Huangpujiang River, China. Benskin et al. (2011) studied the source of perfluorinated carboxylic acids in remote alpine lake sediment cores, and suggested that contributions of perfluorooctanesulfonyl fluoride-based substances and direct transport of perfluorooctanoic acid (PFOA) were ruled to be minimal, while fluorotelomer alcohol oxidation is the dominant atmospheric source of perfluorinated carboxylic acids for these high alpine lakes.

The Haihe River is the largest water system in North China; it flows through Tianjin City to Bohai Bay. The State Council Information Office of China reported that the Haihe River is the most polluted river in China. However, little is known about the vertical variations of sediment cores in this river. In this study, the levels and vertical variations of six PFASs in Haihe River sediment (0–56 cm) were studied; studied substances included PFOA, perfluorononanoic acid (PFNA), PFOS, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), and perfluorododecanoic acid (PFDoA). Samples were collected from the main stream of the Haihe River and two tributaries including the Ziya River and Beiyun River.

## 1. Materials and methods

### 1.1. Study area and sample collection

The Haihe River has five main tributaries, including the Southern Canal, Northern Canal, Ziya River, Daqing River, Beiyun River and Yongding River. The main stream of the Haihe River flows through Tianjin City and empties into the Bohai Sea, with a full length of about 73 km (Hu et al., 2011; Sun et al., 2012). The Haihe River basin has a mean annual precipitation of about 539 mm with mean annual relative humidity between 50% and 70%. Due to a temperate semi-humid and semi-arid continental monsoon climate, the Haihe basin has a windy winter and a dry spring.

In September of 2010, a total of 12 top-sediment samples (0–10 cm) were collected with a hand piston sediment sampler ( $\Phi = 6$  cm) in the sampling stations placed at least 5 m off the Haihe River bank. A GPS was used to record the coordinates of the sample locations. The sampling locations are shown in Fig. 1. S1 and S2 are located at Ziya River, and S3 is on the Beiyun River. Both Ziya River and Beiyun River are on the upstream portion of the main stream of the Haihe River. S2–S6 is in Tianjin City and S4–S6 is on the main stream of the Haihe River. S7–S12 is in the section of the Haihe River downstream of Tianjin City, while S12 is near the Bohai Sea. At the same time, three sediment cores (0–56 cm) were collected in S6, S8 and S11 with a sediment corer with an internal diameter of 57 mm and a length of 1 m. All the samplers were pre-cleaned with methanol and Milli-Q water before sampling, and all the sediment samples

were stored in polypropylene (PP) bottles to avoid contamination and transported to the laboratory immediately.

### 1.2. Chemicals

PFOS (98%) was purchased from Tokyo Chemical Industries (Tokyo, Japan); PFOA (96%), PFNA (97%), PFDA (98%), PFUnA (95%) and PFDoA (95%) were obtained from Acros Organics (Morris Plains, NJ, USA). The physicochemical parameters of the PFASs are listed in Table 1. [1,2,3,4- $^{13}\text{C}_4$ ]Perfluorooctanoic acid (MPFOA) (purity > 99%) was obtained from Wellington Laboratories (Guelph, Canada), and it was used as an internal standard. Methanol of chromatography grade was purchased from J.T. Baker (Phillipsburg, NJ, USA). Ammonium acetate (98%), methyl-tert-butyl ether (99.5%) and tetrabutylammonium hydrogensulfate were purchased from Sigma-Aldrich Chemical Co. (St. Louis, USA), and they were used to extract PFASs from sediment.

### 1.3. Sample preparation and analysis

Sediment samples were dried in a shady place at room temperature, and the debris was removed from them. Then the samples were sieved with a 0.83 mm mesh and transferred into PP bottles until extraction. The PFASs in sediment were extracted by the ion-pairing agent extraction method employed by Stock et al. (2007) with some modifications. In brief, 5 g of sediment sample was weighed and transferred into a 50 mL PP centrifuge tube, and moistened by adding 2 mL cleaned Milli-Q water with vortexing. A total of 2 mL of sodium carbonate buffer (0.25 mol/L), 2 mL of tetrabutyl-ammonium hydrogen sulfate (0.5 mol/L, adjusted to pH 10) and 100  $\mu\text{L}$  (10 ng) of MPFOA, the internal standard, were added into the tube for extraction in turn by vortexing. Subsequently, 5 mL of methyl-tert-butyl ether was added to the bottle and shaken for 30 min; then the bottle was centrifuged for 30 min at 3500 r/min and the supernatant was collected. This extraction process was repeated twice. The supernatants were combined into a 15 mL PP centrifuge tube and the methyl-tert-butyl ether solvent was blown to dryness under a gentle flow of high purity nitrogen. The analytes were dissolved in 1 mL of 80:20 (V/V) methanol:water solution and filtered through a 0.22 mm nylon filter for determination.

PFASs were analyzed by liquid chromatography–tandem mass spectrometry (LC-MS/MS; API 3200 triple quadrupole mass spectrometer (Applied Biosystems, USA) linked to an Ultimate 3000 HPLC (Dionex, USA)) in electrospray negative ionization mode. The method was employed in our previous study (Dai et al., 2012). Briefly, a 10  $\mu\text{L}$  aliquot of extract was injected into a Acclaim 120 C18 Column (5  $\mu\text{m}$ , 4.6  $\times$  150 mm, Thermo Scientific, USA) with 50 mmol/L ammonium acetate and methanol as mobile phase at a flow rate of 1 mL/min, and the mobile phase gradient was ramped from 70% to 95% methanol in 4 min, held at 95% methanol for 3 min, and then ramped down to 70% methanol in 3 min.

The total organic carbon (TOC) of the sediment samples was also as follows. The samples were ground with an agate mortar to pass through a 100 mesh stainless steel sieve, and an elemental analyzer (Vario El, Elementar Analysensysteme GmbH, Hanau, Germany) was used for the TOC analysis after the samples were treated with HCl (1:1, V/V).

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