



Spatial distribution and historical deposition behaviors of perfluoroalkyl substances (PFASs) in sediments of Lake Chaohu, a shallow eutrophic lake in Eastern China



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ABSTRACT

Sediment samples were collected from the Chaohu Lake basin to investigate the spatial distribution and historical deposition behaviors of 17 perfluoroalkyl substances (PFASs). Concentrations of the total PFASs (\sum PFASs) in limnetic sediments ranged from 0.719 to 2.429 ng/g dry weight (dw), with an average of 1.449 ng/g dw. A clear gradient in the spatial distribution was observed from west to east in surface sediments of Lake Chaohu. Perfluorooctane sulfonic acid and perfluorooctanoic acid were predominant in limnetic sediments, with an average of 0.383 and 0.275 ng/g dw, respectively. The \sum PFASs concentrations in riverine sediments were the highest in the Shiwuli River, followed by the Nanfei River. PFASs in riverine sediments indicated that industrial discharge and urban runoff played key roles in PFAS distribution and pollution levels. In vertical profiles, concentrations of the \sum PFASs and PFAS congeners in three sediment cores generally increased with decreasing depths, indicating that the input history of the \sum PFASs could be attributed to the development of industrialization and urbanization in the Chaohu Lake basin. The correlations between PFASs and sedimentary characteristics, organic carbon, nutrients and inorganic salts suggested that both hydrophobic and electrostatic effects played important roles in PFAS distribution and pollution levels in sediments of Lake Chaohu.

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1. Introduction

The production and usage of perfluoroalkyl substances (PFASs) have sharply increased for a wide array of industrial, commercial and consumer goods applications since the late 1940s (Kim et al., 2012). PFASs have been found to be ubiquitous in land (Zareitalabad et al., 2013), oceans (Ahrens et al., 2009a), polar regions (Schenker et al., 2008), wildlife (Loi et al., 2011) and humans (Zhang et al., 2013). Due to their persistence, bio-accumulative properties and potential toxicity, PFASs become environmental contaminants that have already attracted great concern globally. In May 2009, the United Nations Environment Programme officially classified “perfluorooctane sulfonate” and its salts as persistent organic

pollutants (POPs) at the Conference of the Parties 4 of the Stockholm Convention (Buck et al., 2011). PFASs can be released into the aquatic environment from direct sources such as the manufacturing of PFASs and the use of products containing PFASs through various pathways, as well as indirect sources such as the degradation of precursors (Kim et al., 2012; Kim and Kannan, 2007; Prevedouros et al., 2006). It was inferred that a large proportion of emissions would be released to the surface waters, and that sediment burial is one of the most important environmental sinks for PFASs, implying a very long residence time in the environment (Prevedouros et al., 2006). The vertical variations of PFAS concentrations in sediments with depth are able to illustrate the temporal trends of PFASs in sediments. Thus, studies on PFASs in sediments are of great importance.

The occurrence of PFASs in sediments has been found in several countries and areas such as the Pearl River Delta (Liu et al., 2014; Pan et al., 2014a; Zhao et al., 2014), Yangtze River (Pan et al., 2014b; Pan and You, 2010), and Bohai Sea in China (Gao et al., 2014; Wang et al., 2011; Zhu et al., 2014), the Cantabrian Sea in north Spain (Gomez et al., 2011), Tokyo Bay in Japan (Ahrens et al., 2009b), and

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three lakes in the Canadian Arctic (Stock et al., 2007). PFAS concentrations in sediments varied greatly, ranging from below the limits of detection (LODs) to several hundred nanograms per gram of dry weight (dw). Several studies on PFASs in limnetic sediments of China have also been reported, such as Lake Tangxun (Zhou et al., 2013), Lake Taihu (Pan et al., 2014c; Yang et al., 2011), and Lake Baiyangdian (Shi et al., 2012). However, the available studies concerning PFASs in limnetic sediments of China are still scarce as a whole, especially those regarding the historical deposition behaviors of PFASs in sediment cores. Vertical distribution of PFASs in sediment cores, which clearly differed from the “classical” pollutants, was influenced by various factors, such as the carbon chain length of PFASs and the functionality of their head groups (Ahrens et al., 2009b), metal ions (Chen et al., 2012), particle sizes (Zhao et al., 2012) and total organic carbon (TOC) (Ahrens et al., 2009b). The factors influencing PFAS distribution in limnetic sediments also need to be further investigated.

Lake Chaohu (31°25′–31°43′ N, 117°16′–117°51′ E), one of the five largest freshwater lakes of China, is situated in Anhui Province of eastern China and is a typical semi-enclosed shallow eutrophic lake. In recent decades, the land-use pattern in the Chaohu Lake basin has experienced the conversion of agricultural land to industrial and urban land. Since 1950, the urban population of the Chaohu Lake basin has greatly increased from approximately 200 000 people to approximately 1 600 000 by 1985, and then 8 000 000 by 2009. Quantities of fertilizer use have also rapidly increased, accelerating the inputs of agricultural runoff in the catchment. Due to the increasing anthropogenic activities in the Chaohu Lake basin, the lake has suffered from severe pollution and eutrophication, and there is a trophic gradient between the two half-lake regions (Zan et al., 2012). Previous studies performed in Lake Chaohu have mainly focused on nitrogen and phosphorus (Zan et al., 2012), heavy metals (Zan et al., 2011), polycyclic aromatic hydrocarbons (Li et al., 2014), and polybrominated diphenyl ethers (Wang et al., 2013). Information on PFAS concentrations, however, has not been available for Lake Chaohu until now.

The aims of this study were to (1) investigate PFAS levels and spatial distribution in sediments from the Chaohu Lake basin; (2) trace the historical evolution of PFASs in sediments of Lake Chaohu over nearly 60 years; and (3) elucidate the relationship between PFAS concentrations and various influencing factors in sediments of Lake Chaohu.

2. Material and methods

2.1. Study area and sampling

Lake Chaohu has a surface area of 780 km², a mean depth of approximately 3 m and a catchment area of 12 938 km² (Fig. 1). The western region (ca. 1/3 of lake area) is mainly surrounded by Hefei City (the capital city of Anhui Province) and the eastern region (ca. 2/3 of lake area) by Chaohu City. Seven main inflowing rivers, including five rivers were located in the western lake region and two rivers were located in the eastern lake region, account for more than 80% of the runoff volume of the Chaohu Lake basin (Wang et al., 2013). The rivers Nanfei, Shiwuli, and Paihe are the three most polluted rivers within the territory of Hefei City. Two large wastewater treatment plants are situated beside the Nanfei River and the Shiwuli River. The rivers Hangbu and Fengle hold the largest water flows and join together downstream.

A total of 28 surface sediment samples (top 0–5 cm) were collected using a stainless steel grab sampler from the Chaohu Lake basin in December 2011. Sixteen sampling sites were located in Lake Chaohu. Two sampling sites were situated in Lake Wanfohu as the background region. Ten surface sediment samples were

collected along the five main inflowing rivers (Fig. 1). Detailed information is given in the supplementary information (SI) and is listed in Table SI-1. The sediment cores were collected using a hand-driven stainless steel corer (50 cm long and 8 cm i.d.) at M1, M2 and M3 in July 2009 and sliced at 2 cm intervals up to 20 cm after siphoning the overlying water. The three sediment core samples from M1, M2 and M3 were named core-1, core-2 and core-3, respectively. All of the sediment samples were stored in polypropylene (PP) bags after removing the sundries and were kept in freezers. The samples were then immediately transferred to the laboratory and stored at –20 °C until analyzed.

2.2. Chemicals and standards

The internal standards of sodium perfluoro-1-[1,2,3,4-¹³C₄] octanesulfonate (¹³C₄-PFOS, MPFOS) and perfluoron-[1,2,3,4-¹³C₄] octanoic acid (¹³C₄-PFOA, MPFOA) and a mixture of 17 native perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAAs) were purchased from Wellington Laboratories (Guelph, Ontario, Canada) (see Table 1 for details). All stock standards and solutions were prepared in methanol (HPLC grade, Fisher Scientific, Hampton, NH, USA) and stored in PP tubes or vials at 4 °C. Ammonium acetate (HPLC grade), ammonium hydroxide (NH₄OH, HPLC grade; v/v, 50%) and acetic acid (HPLC grade, >99.8%) were purchased from Alfa (Ward Hill, MA, USA). Copper powder (analytical grade, <75 μm, 99.9%) was purchased from Aladdin Industrial Corporation (China). Other chemicals used in the study were of reagent grade and were used as received. Solid phase extraction (SPE) columns (Oasis[®] WAX, Weak Anion Exchange, 6 cc, 150 mg, 30 μm) were purchased from Waters Corporation (Milford, MA, USA). Ultrapure water (18.2 MΩ·cm) provided by Milli-Q Advantage A10 system (Millipore, Billerica, MA, USA) was used for all of the experiments.

2.3. Sample pretreatment

All sediment samples, except for the sub-samples for particle size analysis, were freeze-dried, homogenized and passed through a 150 μm stainless steel mesh sieve prior to analysis. The samples were pretreated as described elsewhere with some minor modifications (Zhou et al., 2013). In general, 2 g of the sediment samples with 1 ng of internal standards were sonicated in 30 mL of methanol at 60 °C for 30 min. For the elimination of sulfur in sediments, activated copper powder was added before the extraction. After shaking for 16 h at a rate of 250 r/min and centrifugation, the supernatant was concentrated to 0.5 mL under a gentle nitrogen stream and diluted to 50 mL with ultrapure water. The dilution was then loaded onto an Oasis[®] WAX single-use cartridge, which was preconditioned with 4 mL of 0.1% NH₄OH (in methanol), 4 mL of methanol and 5 mL of ultrapure water. Cartridges were washed with 4 mL of 25 mmol/L buffer solution (pH 4) and then centrifuged at 3000 r/min for 10 min to remove the residual water. Target compounds were then eluted with 4 mL of methanol and 4 mL of 0.1% NH₄OH (in methanol). The eluent was concentrated to 200 μL under a gentle nitrogen stream for injection.

2.4. Instrumental analysis

Analyses were performed for 17 PFASs using ultra-high performance liquid chromatography (UPLC, Waters Corporation, Milford, MA, USA) equipped with an electrospray ionization tandem mass spectrometer (ESI/MS/MS, Xevo TQD, Waters Corporation, Milford, MA, USA) operated in negative ion and MRM mode. PFASs were separated on an Acquity UPLC[®] BEH C18 column (2.1 mm × 50 mm, 1.7 μm) with an aliquot of 10 μL injections. Nitrogen was used as

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