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Residues, bioaccumulations and biomagnification of perfluoroalkyl acids (PFAAs) in aquatic animals from Lake Chaohu, China

Wenxiu Liu, Wei He, Jingyi Wu, Ning Qin, Qishuang He, Fuliu Xu*

MOE Laboratory for Earth Surface Processes, College of Urban & Environmental Sciences, Peking University, Beijing 100871, China

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ABSTRACT

Residual levels of perfluoroalkyl acids (PFAAs) in seven species of aquatic animals were analyzed by liquid chromatography-mass spectrometry. The distribution, composition, bioaccumulation, and biomagnification of PFAAs and their effect factors were studied. The results showed that: 1) Wet weight concentrations of 17 PFAAs in the aquatic animals ranged from 1.77 to 38.65 ng/g, with a mean value of 12.71 ± 9.21 ng/g. PFOS was the predominant contaminant (4.57 ± 4.57 ng/g, 6.76%–46.25%), followed by PFDA (1.95 ± 1.37 ng/g, 11.68%–21.25%) and PFUdA (1.84 ± 1.21 ng/g, 9.73%–35.34%. 2) PFAA residual levels in *Culter erythropterus* (30.98 ± 6.65 ng/g) were the highest, followed by *Hemibarbus maculatus* (16.79 ± 1.88 ng/g), while the PFAA levels in *Carassius auratus* were the lowest (2.22 ± 0.60 ng/g). 3) Biota-water bioaccumulation factors (BAFs), biota-suspended solid accumulation factors (BSSAFs) and biota-sediment accumulation factors (BSAFs) ranged from 0.35 to 12,370.51, 7.77 to 8452.92 and 9.10 to 6984.61, respectively. Bioaccumulation by shrimp and snails was significantly affected by Kow. 4) Food web magnification factors were greater than 1, indicating that biomagnification of PFAAs occurs across trophic levels. The bioaccumulation and biomagnification of PFAAs were significantly correlated with carbon chain length.

1. Introduction

Typical perfluorinated compounds, perfluoroalkyl acids (PFAAs), including perfluorosulfonic acids (PFSAs) and perfluoalkyl carboxylic acids (PFCAs), are forms of organic acids, with all of the hydrogen atoms in the carbon chain substituted by fluorine atoms. These compounds are stable and persistent; therefore, they are difficult to degrade and metabolize by vertebrates (Key et al., 1997; Kissa, 2001). Prior studies have shown a strong inhibitory effect of perfluorooctanesulfonate (PFOS) and most PFCAs on algae, such as *Chlorella vulgaris*, and they can significantly affect the population (Desjardins et al., 2001; Boudreau et al., 2003; Sanderson et al., 2003). Toxicity was doubled with an increase of additional fluoromethylidene chain length PFAAs (Latala et al., 2009). perfluorooctanoic acid (PFOA) can disturb estrogen activity by inducing estrogen-responsive genes in the male rare minnow (Wei et al., 2007). PFOS can alter gene expression in the hypothalamus-pituitary-thyroid axis of zebrafish and disrupt thyroid hormone synthesis (Shi et al., 2009), and, as a chemosensitizer, can inhibit zebrafish efflux transporter activity (Keiter et al., 2016).

PFAAs can bioaccumulate and biomagnify at successively higher trophic levels of the food web (Giesy and Kannan, 2001). Studies have shown that the bioaccumulation factor (BAF) of PFOS in fish ranged from 274 to 41,600 in several water bodies in Japan (Taniyasu et al., 2003). Conder et al. summarized previous studies, suggesting that bioconcentration and bioaccumulation of PFAAs were directly related to carbon chain length, and PFSAs were more easily bioaccumulated than PFCAs (Conder et al., 2008). perfluorohexanesulfonate (PFHxS) has an exemption half-life time, which is longer than PFOS, however, a linear relationship between bioaccumulation factor (BAF) of PFSAs and carbon number was reported. The BAF value of PFHxS was lower than that of PFOS (Kwadijk et al., 2010; Bhavsar et al., 2016). BAF value was both related to the exposure concentration of PFAAs and the carbon chain length (Liu et al., 2011). Additionally, studies have shown that the biomagnification of PFAAs increases through the trophic levels of the food chain in Lake Ontario and Sarasota Bay (Martin et al., 2004; Houde et al., 2006). The bioaccumulation and biomagnification phenomenon of PFAAs existed in freshwater and marine ecosystems, such as Taihu Lake and Laizhou Bay (Yang et al.,

* Corresponding author.
E-mail address: xufl@urban.pku.edu.cn (F. Xu).

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2012; Xu et al., 2014). However, compared with the biota-water bioaccumulation factors (BAFs) of PFAAs, the biota-suspended solid accumulation factors (BSSAFs) and biota-sediment accumulation factors (BSAFs) of PFAAs are not well documented. More studies on bioaccumulation and biomagnification of PFAAs might be necessary for better understanding of the transfer and fate of PFAAs in freshwater ecosystems.

Lake Chaohu is the fifth largest freshwater lake in China. It not only serves many functions, such as shipping, fishery, irrigation and flood control but is also an important water source for the residents of Hefei and its surrounding cities and towns. In recent years, with increasing discharges of domestic sewage and industrial wastewater, a serious deterioration of lake water quality has had a direct impact on drinking water safety and industrial and agricultural production by residents along the lake. Previous studies have shown that many persistent organic pollutants (POPs), such as PAHs, OCPs, BDEs, PFAAs and other persistent organic pollutants, were detected in Lake Chaohu (Qin et al., 2013; Liu et al., 2012; Liu et al., 2015; He et al., 2013, 2014a; 2014b). However, there is a lack of research on PFAAs and their bioaccumulation and biomagnification in aquatic organisms in Lake Chaohu. The main research goals of this study are to determine the following: 1) residual levels of PFAAs in aquatic organisms of Lake Chaohu; 2) BAF, biota-sediment accumulation factor (BSAF) and biota-suspended solid accumulation factor (BSSAF) of PFAAs in Lake Chaohu aquatic organisms and their effects; 3) biomagnification of PFAAs in Lake Chaohu and its effects.

2. Material and methods

2.1. Sample collection

Seven species of aquatic animals of differing sizes in Lake Chaohu were collected, including five species of edible freshwater fish, one species of shrimp, and one species of snail (shown in Table S1 in the supplementary material). After being delivered to a temporary laboratory, the samples were pretreated the same day. To reduce individual differences, the muscles on both dorsal sides and the chest from three to five conspecific fish were combined into one mixed sample. A total of three, replicate, mixed samples were obtained for each fish species. After the wet weight was obtained, the samples were freeze-dried, weighed for dry weight and ground into a granular powder with a ball mill (MM400, Retsch GmbH, Germany). The amber glass bottles that contained the sample powder were sealed in a dryer until analyzed.

Water samples from Lake Chaohu were collected from twenty sampling sites (Fig. S1 in the Supporting Information). After shaking and mixing, one liter of water sample was filtered through a 0.45 μm glass fiber filter (GFF) membrane using a peristaltic pump (80EL005; Millipore Co., USA) and a filter plate with a diameter of 142 mm to separate the suspended solids. The GFF membrane was ashed at 450 °C for 4 h before use. 5 ng of an internal standard (including [1,2,3-$^{13}C_3$]PFHxS、[1,2,3,4-$^{13}C_4$]PFOS、[1,2,3,4-$^{13}C_4$]PFBA、[1,2,3,4-$^{13}C_4$]PFOA、[1,2-$^{13}C_2$]PFDoA, Wellington Labs, Ontario, Canada) was added to the water.

Suspended solids were collected by the GFF membrane filtering the water. The weight difference of the GFF membrane before and after filtering represented the quantity of suspended solids.

A grab sampler was used to collect the surface sediment samples from 18 sampling sites (excluding L1 and R2). The samples were stored in sealed bags and frozen at −20 °C in a refrigerator until treatment. After the sediment samples were freeze-dried, the samples were ground into powder and sieved through a 200 mesh sieve.

2.2. Extraction and cleanup

A total of 0.5 grams of freeze-dried biota samples were weighed into 15 mL polypropylene centrifuge tubes and 5 ng of internal standard, 1 mL of tetrabutylammonium hydrogen sulfate aqueous solution (TBAS, 0.5 mol/L), and 2 mL of aqueous sodium carbonate (0.25 mol/L, pH = 10) were added. Then, 5 mL of MTBE were added to the tubes. After being vortexed for 15 min and centrifuged for 10 min, the supernatant was transferred to a clean tube and the process repeated two more times. The supernatants were combined and dried under high purity nitrogen, and redissolved in 1 mL of methanol. The 1 mL sample was passed through an ENVI-CARB cartridge (3 mL, 250 mg, Sigma-Aldrich Co., USA) and eluted three times with 1 mL of methanol. The eluate was collected and diluted to 100 mL with ultrapure water, and loaded on an OASIS WAX cartridge (6 mL, 150 mg, Waters Corp., USA), which was preconditioned sequentially with 4 mL 0.1% NH_3OH methanol solution, methanol, and ultrapure water. After the extraction, the cartridge was washed with 4 mL of ammonium acetate buffer (pH 4.0, 25 mM), and eluted with 4 mL of methanol and 4 mL of 0.1% Ammonium hydroxide (NH_4OH) in methanol. The eluate was concentrated to 1 mL under the nitrogen, and filtered with a polypropylene syringe filter (GHP, 13 mm, 0.2 mm, Pall Corp., USA) into a 2 mL brown, glass vial with a 200 μL insert and polyethylene (PE) septa.

The water samples were extracted according to the method published by Liu et al. (2015). The extraction of suspended solids and sediment samples was followed by a published method with some modifications (Higgins et al., 2005; Nakata et al., 2006). The GFF membrane or 8 g of sediment was placed in a 50 mL centrifuge tube, and 5 ng of internal standard was added. Then, 30 mL of methanol was added as solvent, and sonicated for 20 min. The process was repeated two more times, and the supernatants were combined and concentrated to 1 mL using a vacuum rotary evaporator. Then, the following procedure of cleanup and extraction was same as the method of biota samples.

2.3. The instrument analysis and quality assurance

A published method was used to analyze PFAAs (Wang et al., 2014). Seventeen PFAAs, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA), potassium perfluorobutanesulfonate (PFBS), sodium perfluorohexanesulfonate (PFHxS), potassium perfluorooctanesulfonate (PFOS), and sodium perfluorodecanesulfonate (PFDS), were detected. The samples were analyzed using an Agilent 1290 Infinity HPLC System coupled with an Agilent 6460 triple quadrupole LC/MS System (Agilent Technologies, Palo Alto, CA). A Zorbax Eclipse Plus C18 column (2.1 × 100 mm, 3.5 μm, Agilent Technologies, Palo Alto, CA) was used, with a column temperature of 40 °C, and 5 μL sample was injected. Ammonium acetate solution at 2 mM (solvent A) and acetonitrile (solvent B) were used as mobile phases at a flow rate of 0.3 mL/min, starting with 80% A and 20% B. This condition was held for 13 min, then increased to 90% B for 14 min. The source gas (N2) flow rate and temperature were maintained at 9 L/min and 350 °C, respectively. ESI-MS measurement was performed in negative MRM detection mode. The capillary voltage was 3500 V. Polytetrafluoroethylene (PTFE) and other fluorinated materials were