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Elevated concentrations of perfluorohexanesulfonate and other per- and polyfluoroalkyl substances in Baiyangdian Lake (China): Source characterization and exposure assessment☆

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ABSTRACT

Novel 6:2 chlorinated polyfluorinated ether sulfonate (6:2 Cl-PFESA) and legacy PFASs, such as perfluorohexane sulfonate (PFHxS), have been used to replace perfluorooctane sulfonate (PFOS), a known persistent organic pollutant. Thus, it is critical to understand these PFOS alternatives regarding their sources and concentrations in the natural environment. In this study, 41 surface water samples as well as edible aquatic organisms were collected from Baiyangdian Lake, the largest freshwater lake in Hebei Province, China. Perfluorooctanoate acid (PFOA) and PFHxS were the predominant PFASs detected in the surface water, reaching concentrations of 8 397.23 ng/L and 1 478.03 ng/L, respectively, with PFHxS accounting for the greatest proportion (~80.00%) in most water samples. PFHxS (mean: 87.53 ng/g) and PFOS (mean: 35.94 ng/g) were also the most prevalent compounds detected in aquatic organisms. Estimated daily intake (EDI) values of PFOS (16.56 ng/kg bw/d) and PFHxS (16.11 ng/kg bw/d) via aquatic food and drinking water were the highest among PFASs, indicating potential exposure risks to residents. In addition, fish product consumption was the important exposure pathway for residents to PFOA, PFHxS, PFOS, and 6:2 chlorinated polyfluorinated ether sulfonate (6:2 Cl-PFESA). This study reports on the highest PFHxS levels ever recorded in surface water, suggesting that further quantification of PFHxS in human serum and assessment of its health risks to local residents are warranted and critical.

1. Introduction

Poly- and perfluoroalkyl acids (PFASs) have been widely used as additives in products such as food packaging, flame retardants, textiles, and carpets due to their unique water and oil resistant properties (Giesy and Kannan, 2001, 2002; Lindstrom et al., 2011). However, due to their persistent characteristics, PFASs can accumulate in the environment (Chen et al., 2016; Yeung et al., 2017; Zhao et al., 2017), wildlife (Yeung and Mabury, 2013), and human body (Olsen et al., 2003; Poothong et al., 2017), resulting in adverse risks to animals and humans from polluted aquatic ecosystems (Squadrone et al., 2014; Wu et al., 2012). Increasing concern regarding the persistency, bioaccumulation, and toxicity of PFASs, especially long-chain compounds such as perfluoroalkyl carboxylic acids (PFCAs, $C_nF_{2n+1}COOH$, $n \geq 7$) and perfluoroalkane sulfonic acids (PFSAs, $C_nF_{2n+1}SO_3H$, $n \geq 6$) resulted in the voluntary discontinuation of perfluorooctanesulfonate (PFOS) production by its largest manufacturer in 2000 (3M 2000). Furthermore, in May 2009, the Stockholm Convention included PFOS and its salts as Persistent Organic Pollutants, thereby advising regulation of their production and use (UNEP, 2009). Consequently, manufacturers have been committed to finding nonregulated alternatives. According to Wang et al. (2015b), PFOS and its relevant chemicals have been primarily replaced by two groups of fluorinated alternatives, namely, short-chain PFSAs ($CF_2 \leq 6$) and perfluoroether sulfonic acids (PFESAs).

PFHxS, which exhibits lower toxic potency than PFOS (Buhrke et al., 2013), has been frequently observed in the environment; furthermore, several studies have inferred that PFHxS is increasingly used and produced due to the regulation of PFOS (Ma et al., 2018). However, PFHxS has been detected in human serum at considerable concentrations, with only PFOS and PFOA found at higher levels (Hemat et al., 2010). Increasing PFHxS concentrations in human serum over time have also been reported (Glynn et al., 2012; Kato et al., 2011). Several studies have revealed that PFHxS

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has a similar serum elimination half-life as that of PFOS in tested mice (Chang et al., 2012; Sundstrom et al., 2012), and possibly longer in human serum (Olsen et al., 2007). Due to its adverse effects and increasing levels in different biota, especially human matrices, as well as its long half-life in human serum, PFHxS, its salts, and related compounds have been added to the candidate list of substances of very high concern by the European Chemicals Agency and fit the requirements of Annex D of the Stockholm Convention (ECHA, 2017; Stockholm Convention, 2017). For PFESAs, predominant 6:2 Cl-PFESA has been used in the chrome plating industry in China for over 30 years as a PFOS alternative, and has since been detected in water, wildlife, and humans (Gebbink et al., 2016; Xiao, 2017; Pan et al., 2018). Several studies have suggested that 6:2 Cl-PFESA is hard to bio degrade and exhibits a higher bioaccumulation potential than PFOS (Shi et al., 2015; Wang et al., 2013).

The counties of Anxin and Xiong, located within the Xiong'an New Area approximately 100 km southwest of Beijing, are special economic zones that undertake non-capital functions that have shifted from Beijing. Baiyangdian Lake, the largest freshwater lake in Anxin County, maintains the ecological balance in this region and supplies important natural resources to the surrounding population (364 800 people). Previous research reported on 12 PFASs detected in the surface waters (mean: 19.80 ng/L) of Baiyangdian Lake prior to 2008 and revealed that PFAS contamination was relatively low compared to that from Tangxun Lake (mean: 9 850.00 ng/L) and Taihu Lake (mean: 102.00 ng/L) in China (Yu et al., 2013; Zhou et al., 2013; Shi et al., 2012). However, due to the rapid industrial and economic development of the cities surrounding this lake, substantial manufacturing and domestic wastewaters from Baoding, an important industrial city, have been directly discharged into the lake through Fu River transport (Wang et al., 2014), with persistent pollutants, such as PFASs, thereafter stored within the lake waters for prolonged periods. To date, however, limited knowledge is available regarding variation in the levels of both legacy and alternative PFASs following this rapid industrialization. Therefore, investigation on the levels and temporal variations of such PFASs in Baiyangdian Lake is essential.

Dietary intake is one of the main PFAS exposure pathways for humans (Fromme et al., 2009); furthermore, freshwater fish consumption is the primary pathway of PFOS exposure among foodstuffs (Ericson et al., 2008; Haug et al., 2010). As aquatic products occupy a vital position in the local diet, the potential hazard to residents who consume wild-caught aquatic foods from Baiyangdian Lake is of particular concern. Thus, assessing local population exposure to PFASs via consumption of aquatic organisms and drinking water is crucial. The main objectives of this study were to: (1) investigate the concentration and variation of PFASs as well as PFAS alternatives, in surface water and aquatic organisms from Baiyangdian Lake; (2) identify potential emission sources of PFASs in surface water using principal component analysis; and (3) evaluate the exposure levels of individual PFASs to residents via aquatic product and drinking water consumption.

2. Materials and methods

2.1. Study area and sample collection

Baiyangdian Lake is the largest freshwater wetland in Hebei Province, China, into which the Fu, Zhulong, and Baigouyin rivers flow from three different directions and out of which water flows into Zhaowangxin River. In the present study, a total of 41 surface water samples from Baiyangdian Lake and these rivers (Fig. 1), as well as two tap water samples, were collected in August and September 2016. Tap water pumped from one well is used for drinking water by the local population. After the sampling campaign, ten water samples were collected near the F7–11 and ZL1–5 sites in April 2018 to ensure the repeatability of the data. Water samples were collected at 0.5 m below the surface using a water sampler in 1-L polypropylene (PP) bottles rinsed with methanol before use. All samples were maintained at −20 °C until further analysis. Details on sampling locations and dates are given in Table S1 of the Supplementary Information (SI).

Two sampling surveys for edible aquatic products were conducted at four sites located in different regions of Baiyangdian Lake in August 2016 and April 2018 (Table S2). The 11 collected fish species, which included most species consumed and most species inhabiting the lake, were captured by local fishermen using fishnets. Three crab and several shrimp species were also collected. Four free-range ducks raised around Baiyangdian Lake and ten duck eggs were collected from two local duck farms. For biota, 50-mL PP tubes were used to hold samples. The individual shrimp samples were whole-body homogenized. Fish, ducks, and crabs were carefully dissected to obtain edible muscle and other tissues (e.g., duck liver, duck blood, crab spawn), which were subsequently homogenized and then stored at −20 °C until further use. Detailed information, including sampling locations, dates, numbers, and types, are given in Table S2.

2.2. Standards and reagents

The target PFAS analytes included C4–C14 PFCAs, C4, C6, and C8 PFSAs, perfluorooctane sulfonamide (FOSA), ethyl perfluorooctane sulfonamido acetate (EtFOSAA), 4:2, 6:2, and 8:2 Cl-PFESAs, and 6:2 fluorotelomer sulfonate (6:2 FTSA). Detailed information on standards and reagents are described in the contents of the SI.

2.3. Sample extraction

Water samples were extracted by solid-phase extraction (SPE) and fish muscle samples were pretreated by alkaline digestion followed by SPE cleanup, as described previously (Taniyasu et al., 2005). Briefly, 0.5 ng of mixed internal mass-labelled standard was spiked into 200 mL of water, then extracted using an Oasis weak anion exchange cartridge (200 mg/6 mL, Waters, Milford, MA, USA) preconditioned by passing 8 mL of 0.5% ammonium hydroxide in methanol, followed by 4 mL of methanol and 4 mL of ultrapure water. Mixed samples were loaded onto the cartridges, washed with 4 mL of 25 mM ammonium acetate buffer (pH = 4), and eluted separately with 4 mL of methanol and then with 4 mL of 0.5% ammonium hydroxide in methanol. The two fractions were evaporated to dryness under nitrogen gas and were reconstituted using 200 μL of methanol.

Muscle samples (0.20 g) were spiked with 0.50 ng of mass-labelled standard, sonicated for 1 h in 10 mL of 10 mM potassium hydroxide (KOH) methanol solution at 60 °C, and finally shaken overnight at 300 rpm. The supernatant was evaporated to dryness and diluted to 50 mL with water for further SPE cleanup. Other edible samples (except for muscle) were extracted using ion-pair extraction (Hansen et al., 2001) coupled with SPE. Approximately 0.50 g of each sample and 0.50 ng of internal standard were homogenized with 2 mL of 0.25 M sodium carbonate buffer and 1 mL of 0.50 M tetrabutylammonium hydrogen sulfate (TBAS) in 15-mL PP tubes. Subsequently, 4 mL of methyl tert-butyl ether (MTBE) was added to each tube, which were then shaken at 200 rpm for 40 min and centrifuged at 4 400 rpm for 15 min at room temperature, with the upper layers then transferred to new PP tubes. This procedure was repeated twice. The combined solvent was dried under nitrogen gas and then reconstituted to 10 mL using water, with the same procedures used for water extraction then applied.