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Temporal trends and transport of perfluoroalkyl substances (PFASs) in a subtropical estuary: Jiulong River Estuary, Fujian, China

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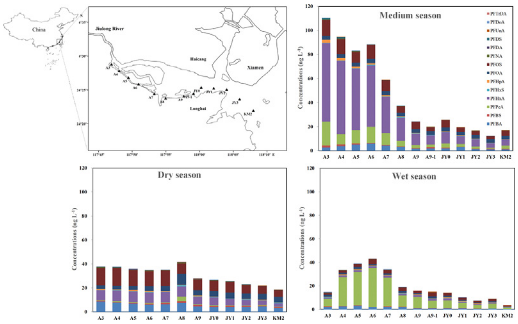
HIGHLIGHTS

- Seasonal and spatial variations of PFASs in a subtropical estuary were presented.
- The predominant PFASs were PFHxA, PFPeA and PFOS.
- The highest concentration of $\sum$PFASs was found in the medium season.

GRAPHICAL ABSTRACT



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ABSTRACT

The seasonal variations and spatial distributions of fifteen perfluoroalkyl substances (PFASs) were investigated in the water of the subtropical Jiulong River Estuary (JRE) in Fujian, China. The concentrations and composition profiles of PFASs showed significant seasonal variations. $\sum$PFASs concentrations ranged from 4.8 to 37.6 ng L^{-1}, 12.2 to 110 ng L^{-1} and 3.3 to 43.0 ng L^{-1} in the dry, medium and wet seasons, respectively. Perfluorooctane sulfonate (PFOS) was found to be the most abundant PFAS in the dry season, with a composition of 33% ± 5%, Perfluorohexanoic acid PFHxA (47% ± 13%) and perfluoropentanoic acid (PFPeA) (52% ± 15%) were the dominant compounds in the medium and wet seasons, respectively. Seasonal and spatial distributions of $\sum$PFASs were different in the upstream and downstream sections. High concentration of PFHxA occurred in the medium season, and showed a linear decreasing trend from upstream to downstream. The majority of other PFASs did not show clear seasonal variation. Composition profiles indicated that the JRE was mainly contaminated by short-chain perfluoroalkyl carboxylic acids (PFCAs), shipbuilding industry, multiple wastewater and river runoff were identified as major potential sources.

1. Introduction

Owing to their surface active properties and high chemical and thermal stability, perfluoroalkyl substances (PFASs) have been used as textile protectors, coatings, plastics, firefighting foams, photolithographic chemicals, electronic chemicals, shampoos, stain repellents for

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furniture, carpets, pesticides and fluoropolymer additives. Due to the highly persistent, bio accumulative and hazardous characteristics, long-chain perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) have attracted global attention. Since 2009, regulations to ban the production and use of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) and their salts have increased in developed countries, (European Commission, 2010; USEPA, 2000; USEPA, 2006). As a consequence of these regulations, the production of long-chain PFASs has shifted toward less regulated countries in Asia as well as toward short-chain PFASs (Krafft and Riess, 2015; Wang et al., 2014b). In recent decades, considerable amounts of PFASs have been detected in various environmental matrices, including water, atmosphere, sediment, wildlife and human tissues (Guruge et al., 2015; Vassiliadou et al., 2015), and relatively high concentrations have been observed in the water of many Asian countries (Takemine et al., 2014; Wang et al., 2016a). Overall, PFOS and PFOA were still the most frequently observed and reported PFASs due to their high production and wide application in fluoropolymer manufacture. In recent studies, PFOA has been found to be the dominant PFAS in North Bohai coastal rivers (Chen et al., 2017), Xiaoqing River (Shi et al., 2015), Huangpu River (Sun et al., 2017), Taihu Lake (Guo et al., 2015) and the surface waters of eastern China (Lu et al., 2015). PFOS has been shown to be dominant in the water of the Pearl River Delta region (Pan et al., 2014a), and Korean rivers and lakes (Lam et al., 2014). However, an increasing number of studies have reported high detection frequencies and concentrations of short-chain PFASs (Chen et al., 2015; Meng et al., 2015; Zhou et al., 2013; Zhao et al., 2017), Fig. S3 and S4 show as a result of the production and use of short-chain perfluorinated alternatives as substitutes for PFOS and PFOA.

The Jiulong River is the second-largest river in Fujian province, with two major tributaries and an average annual freshwater discharge of 1.47×10^{10} m^3 (Zhang, 1996). The Jiulong River Estuary (JRE) is a shallow subtropical estuary with high turbidity in the low salinity region. Due to multiple tributary inputs at its outlet and strong monsoon-driven coastal currents from the Taiwan Strait, the estuary is characterized by intensive interface processes (Guo et al., 2011b). Many studies have confirmed the presence of various contaminants in the JRE, including polycyclic aromatic hydrocarbons (Tian et al., 2008), pesticides (Lin et al., 2013), antibiotics (Zheng et al., 2011) and polybrominated diphenyl ethers (Wu et al., 2017). As the major production base of fluorine chemicals in China, Fujian has attracted much attention for its emission of perfluorinated compounds (PFASs). A previous study (Zhao et al., 2011) determined the levels of PFASs in fish from Xiamen and confirmed the presence of human health risks posed by PFASs via fish consumption. A survey on the PFASs levels in human blood (Yeung et al., 2006) showed that $\sum$PFASs was in the range of 8.84–82.1 ng L^{-1} in Xiamen. The PFOS concentration (maximum 69.9 ng L^{-1}) was higher than that of other coastal cities in China, such as Dalian (Liu et al., 2009), Weihai (Guo et al., 2011a) and Ningbo (Pan et al., 2010). However, data about the occurrence of PFASs in the water of the JRE and how they are transported to the Taiwan Strait are limited.

Riverine levels of PFASs could reflect the emission of PFASs from a watershed and the transport of PFASs to the marine environment. The primary sources of riverine PFASs are industrial or municipal waste water treatment plants (WWTPs) (Becker et al., 2008; D'eon et al., 2009), landfill seepage disposal and spill sites (Busch et al., 2010; Eggen et al., 2010), dry or wet atmospheric deposition (Dreyer et al., 2010; Shan et al., 2015) and discharge by urban runoff contaminated by non-point sources (Murakami et al., 2009; Nishikoori et al., 2011). In addition, atmospheric transportation of volatile fluorinated compounds, such as telomer and perfluorooctane sulfonamide, followed by deposition and degradation, could be potential sources of PFASs (Kwok, 2012). Thus, the objectives of the present study were to (1) investigate the spatial and seasonal variations of PFASs in the water of the JRE, (2) explore the transport behavior of dominant PFASs from the JRE to the coastal area, and (3) identify the pollution sources and evaluate mass flow of PFASs to provide a basis for risk assessment and surface water management.

2. Materials and methods

2.1. Sampling

Sampling was conducted along the JRE network (see Fig. 1). Detailed sampling information is listed in Table S1. Based on the water discharge of the Jiulong River, the wet season is from May to September, the dry season is from December to next February, and the rest of the year is considered to be the "medium" season (Wu et al., 2017). Three sampling campaigns in different seasons were performed at 13 sites in December 2014 (dry season, excluding A9–1), April 2015 (medium season) and August 2015 (wet season). In each cruise, 1 L surface water was collected using a pre-cleaned stainless steel bucket and stored in a 1 L polypropylene (PP) bottle. No glass or Teflon materials were used during the procedure, because PFASs may bind to the glass in aqueous solution and Teflon materials may release PFOA. One mL of sodium thiosulfate (1 mol L^{-1}) was added to each sample to prevent microbial growth. Sample duplicates and field blanks were collected along with the samples and were analyzed with the laboratory and procedural blanks. Samples were preserved under −5 °C immediately in the lab and all samples were extracted within one week of arriving in the lab.

2.2. Reagents and materials

Samples were analyzed for eleven PFCAs and four PFSAs. Standard solutions of $^{13}C_4$-labelled PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnA, PFOS, $^{13}C_2$-labelled PFDoA and $^{18}O_2$-labelled PFHxS were purchased from Wellington Laboratories (Guelph, Ontario, Canada). All stock solutions were prepared in methanol and stored in PP tubes at 4 °C. Other reagents included methanol for HPLC, ≥99.9% (Sigma-Aldrich, USA), ammonium hydroxide for analysis, 25% in water (ACOS Organics, USA), acetic acid, 99.8% (J&K Scientific, China), ammonium acetate (CNW, Germany) and formic acid solution for HPLC, 50% in water (Fluka, USA). Solid-phase extraction cartridges, Oasis® WAX (6 mL, 150 mg, 30 μm), were purchased from Waters (Milford, USA). All laboratory vials and equipment were washed with running water followed by MilliQ (Millipore) water, methanol and dried before use to remove potential PFAS reside.

2.3. Extraction of PFASs

After the water samples (1 L) were equilibrated at room temperature, 500 μL formic acid (50% in water) was added to adjust the pH (5–6). The cartridges were preconditioned by eluting with 4 mL of 0.1% (v/v) NH_4OH solution in methanol followed by 4 mL of methanol and 4 mL of MilliQ water. The water samples were then spiked with 200 μL of 10 ng mL^{-1} of the internal standards and loaded onto the cartridge at a rate of 2–3 drops s^{-1}. The eluent was discarded. The cartridges were then cleaned with 4 mL ammonium acetate buffer (25 mmol L^{-1}, $pH = 4$) and left to dry under vacuum for 15 min. Lastly, the target fraction was eluted using 4 mL of methanol followed by 4 mL 0.1% (v/v) NH_4OH in methanol and collected in a 15 mL PP centrifuge tube. The eluate was then reduced to 0.5 mL under a gentle stream of nitrogen, and made up to a final volume of 1 mL (1:1 methanol/water) for HPLC-MS/MS analysis.

2.4. Instrumental analysis

The extracts were analyzed by a high performance liquid chromatography negative electrospray ionization-tandem mass spectrometry (HPLC-(−)ESI-MS/MS) system using a Agilent 1290 LC coupled to an Agilent 6490 Trip Quadrupole MS (Agilent Technologies, California,