



Spatiotemporal distribution and potential sources of perfluoroalkyl acids in Huangpu River, Shanghai, China



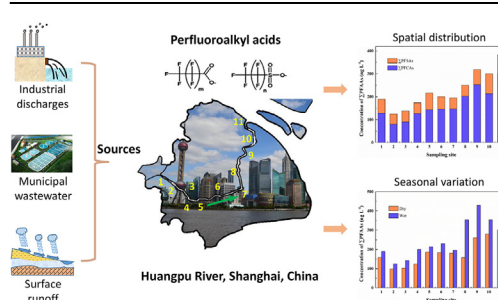
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HIGHLIGHTS

- Perfluoroalkyl acids (PFAAs) in Huangpu River was at a high level on a global scale.
- PFOA and PFOS were dominant while shorter chain length PFAAs were increasing.
- Obvious higher concentrations occurred in the wet season.
- Industrial discharges, municipal wastewater and surface runoff were major sources.
- Great discharge load and hazard assessment indicated severe contaminations.

GRAPHICAL ABSTRACT



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ABSTRACT

Perfluoroalkyl acids (PFAAs) have been found to be ubiquitously disseminated in the environment due to their widespread use in recent decades. In this study, the occurrence and spatiotemporal distribution of PFAAs in the surface water of Huangpu River, Shanghai, China were investigated from 2012 to 2014. The total concentration of 14 PFAAs (Σ PFAAs) ranged from 39.8 to 596.2 ng L⁻¹, with a mean value of 226.3 ng L⁻¹. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) were dominant, with their mean concentrations of 139.6 and 46.5 ng L⁻¹, respectively. The concentration of Σ PFAAs increased greatly downstream especially in the lower reach of an industrial and urbanized area. Samples collected in different seasons were used to analyze the seasonal variation. The results showed that higher concentration of Σ PFAAs occurred in the wet season, especially downstream. Therefore, industrial discharges, municipal wastewater and surface runoff were identified as major potential sources. The annual discharge load of Σ PFAAs from Huangpu River to Yangtze River was estimated to be 2263.4 kg yr⁻¹. The hazard assessment suggested that the contamination of PFAAs in Huangpu River could pose risks to the aquatic environment and drinking water safety, which should draw more attention.

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1. Introduction

Perfluoroalkyl acids (PFAAs) including perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonates (PFASs) are a class of anthropogenic chemicals that contain a hydrophobic alkyl chain with all hydrogen replaced by fluorine and a hydrophilic function

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end group. For over six decades, PFAAs have been manufactured and widely used in various industrial and commercial applications including metal plating and cleaning, coating formulations, fire-fighting foams, varnishes, vinyl polymerization, oil and lubricants, water repellents for leather, paper and insecticide due to their unique physico-chemical properties such as the stability, the ability to lower surface tension, and the hydrophobic and lipophobic properties (Buck et al., 2011; Giesy and Kannan, 2002; Kissa, 2001; Prevedouros et al., 2006). As a result, PFAAs have been detected ubiquitous in many habitats, including indoor and outdoor air, dust, water, sediment, wildlife, human breast milk and blood (Higgins et al., 2005; Kannan et al., 2001, 2004; Shoeib et al., 2005; So et al., 2006; Taniyasu et al., 2003). Studies also suggested the presence of PFAAs in remote regions like the Arctic (Zhao et al., 2012) and the western Antarctic Peninsula (Nash et al., 2010), which was likely to occur through atmospheric or ocean water transport. Toxicological researches have shown that PFAAs are related to the developmental toxicity, immunotoxicity and hepatotoxicity (Lau et al., 2007). Because of the strong strength of carbon-fluorine bonds (~110 kcal/mol), PFAAs exhibit high stabilities in the environment with extreme resistance against chemical and biological degradation (Giesy and Kannan, 2002). Thereby, considering their environmental persistence, bioaccumulation, potential eco-toxicity risks and adverse health effects (Lau et al., 2007; Seacat et al., 2003), quantitative characterization of PFAAs is of great significance.

Due to distinctive production and consumption demands (Kannan et al., 2004; Kunacheva et al., 2012), the occurrence of PFAAs exhibits strong spatial differences among various regions. From 2002, the majority of perfluorooctyl-based production via electrochemical fluorination (ECF) process was ceased by the largest global manufacture, 3M Company (Buck et al., 2011; USEPA, 2000). To accommodate the ongoing domestic and overseas demands in various application fields, PFAAs began to be produced in large quantities in China (Mei, 2008; So et al., 2004). The annual commercial production of perfluorooctane sulfonic acid (PFOS) increased dramatically from 30 t yr⁻¹ in 2001 (Liu et al., 2008), to 220–240 t yr⁻¹ in 2006–2011 (Wang et al., 2015). The production of perfluorooctanoic acid (PFOA) also increased rapidly from 30 t yr⁻¹ in 2004 to 90 t yr⁻¹ in 2012 (Li et al., 2015). The extensive manufacture and use of PFAAs pose great risks to the nationwide environment. Thus, studies on the occurrence of PFAAs have burgeoned gradually on a national scale, especially since PFOS was included in the national priority control list in 2009. However, most of them adopted a single sampling campaign. Little information is available regarding the seasonal variation. Therefore, more researches are still needed.

Shanghai, located in the Yangtze River Delta (YRD), is one of the most prosperous industrial and commercial cities in China, with the highest population density. The Huangpu River is a symbolic river of Shanghai and plays a key role in supplying waters for drinking, production, shipping and irrigation. Also it is one of the primary water bodies for receiving industrial and municipal wastewaters (Zhang et al., 2013a). Therefore, Huangpu River would suffer serious PFAAs contamination. In recent years, high concentrations of PFAAs were found in this area. So et al. (2007) reported a total concentration of 289.2 ng L⁻¹ for PFAAs in the surface water of Yangtze River sampled from a Shanghai location. Mak et al. (2009) investigated the tap water samples collected from 19 cities in 5 countries, and those from Shanghai were found to contain the greatest concentration of ΣPFAAs (mean 130 ng L⁻¹). In our previous studies, high levels were also observed in soils, sediments, wastewater treatment plant (WWTP) effluents and sludge, and landfill leachates in Shanghai (Li et al., 2010; Yan et al., 2015; Zhang et al., 2015). These results indicated that as the major industrial and

financial center in China, Shanghai is one of the most heavily PFAAs-contaminated area. However, no comprehensive investigation on the occurrence of PFAAs in Huangpu River has been reported so far, which is thereby urgent and desirable.

In this study, the concentrations of 14 PFAAs were detected in the surface water of Huangpu River. The objectives of the research are to investigate the occurrence, spatial distribution and seasonal variation of PFAAs in Huangpu River, discern possible sources and evaluate their potential risks to aquatic environments.

2. Materials and methods

2.1. Chemicals and standards

Pentafluoropropionic acid (PFPrA, 97%), perfluorobutyric acid (PFBA, 99%), perfluoroheptanoic acid (PFHpA, 99%), perfluorodecanoic acid (PFDA, 98%), perfluorododecanoic acid (PFDoA, 95%), perfluoro-1-butanefluoronic acid potassium salt (PFBS, 98%) and perfluorooctane sulfonic acid (PFOS, ~40% in water) were obtained from Aldrich Chemical Co. (Milwaukee, WI). Perfluoropentanoic acid (PFPeA, ≥94%), perfluorohexanoic acid (PFHxA, ≥97.0%), perfluorooctanoic acid (PFOA, ≥90%), perfluorononanoic acid (PFNA, ≥95.0%) and perfluorohexanesulfonic acid potassium salt (PFHxS, ≥98.0%) were purchased from Fluka (Buchs, Switzerland). Perfluoroundecanoic acid (PFUnA, 95%) was purchased from Sigma-Aldrich (St. Louis, MO). Perfluorotetradecanoic acid (PFTA, 96%) was provided by Alfa Aesar (Ward Hill, MA). Perfluoro-*n*-[1,2,3,4-¹³C₄]octanoic acid (MPFOA, ≥98%, ¹³C₄) and sodium perfluoro-1-[1,2,3,4-¹³C₄]octanesulfonate (MPFOS, ≥99%, ¹³C₄) were acquired from Wellington Laboratories Inc. (Guelph, ON, Canada). The internal standard MPFOA was used for the quantification of PFCAs, while MPFOS was used for the quantification of PFASs.

Oasis® WAX (6 cc, 150 mg, 30 μm) SPE cartridges were acquired from Waters (Milford, MA). Bulk Envi-Carb sorbent (100 m² g⁻¹, 120/400 mesh) was purchased from Supelco (Bellefonte, PA). HPLC grade formic acid (96%), glacial acetic acid (99.7%) and ammonium acetate (97.0%) were purchased from TEDIA (Fairfield, OH). Ammonium hydroxide solution (25%), and HPLC grade methanol (≥99.9%) were acquired from Sigma-Aldrich. Milli-Q water and deionized water were used throughout the whole experiment.

2.2. Sample collection

The Huangpu River is about 114 km (km) long, which originates from Dianshan Lake and flows east past Shanghai into the Yangtze River at Wusong. About 83 km of the river flows through Shanghai metropolitan area. The upper stream flows through suburban areas mainly dominated by agricultural activities and livestock industries, while the lower stream runs through industrial and urbanized areas with intensive human activities.

Surface water samples (n = 121) were collected from 11 sampling sites (S1–S11) (Fig. 1) along the river. S1 represents the first sampling site in the upper reach. Eleven sampling events were conducted in February, April, June in 2012, February, April, June, August, December in 2013 and February, April, June in 2014. Basically, the sampling events were conducted every two months, except under special circumstances such as bad weather, ship problem, etc. Composite samples were taken from the center of the river cross section at each sampling site, which were transported to the laboratory in 500 mL polypropylene containers within 24 h and stored at 4 °C before analysis. Teflon bottles and Teflon materials were avoided throughout the experiment. Details of the sampling sites are available in Table S1 in Supporting Information (SI).

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