Spatiotemporal distribution and mass loadings of perfluoroalkyl substances in the Yangtze River of China

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HIGHLIGHTS

- Contamination profiles of 18 PFCs in the Yangtze River investigated
- PFOA was the predominant PFAS contaminant both in water and sediment.
- The annual mass loading of total PFASs was 20900 kg/year.
- Wuhan and Er'zhou contributed the most amounts of PFASs into the Yangtze River.
- No significant seasonal variations observed for most PFASs in water.
- Most PFAS concentrations were correlated positively with TN both in water and sediment.

ARTICLE INFO

ABSTRACT

A systematic investigation into contamination profiles of eighteen perfluoroalkyl substances (PFASs) in both surface water and sediments of Yangtze River was carried out by using high performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) in summer and winter of 2013. The total concentrations of the PFASs in the water and sediment of Yangtze River ranged from 2.2 to 74.56 ng/L and 0.05 to 1.44 ng/g dry weights (dw), respectively. The PFAS concentrations were correlated to some selected water quality parameters such as pH, total phosphorus (TP), total nitrogen (TN) and conductivity in water, and some sediment properties, such as total organic carbon (TOC), TP, and TN in sediment. The monitoring results for the water and sediment samples showed no obvious seasonal variations. Among the selected 18 PFASs, perfluorooctanoic acid (PFOA) was the dominant PFAS compound found both in water and sediment for the two seasons with its maximum concentration of 18.03 ng/L in water and 0.72 ng/g in sediment, followed by perfluorobutane sulfonic acid (PFBS) with its maximum concentration of 41.9 ng/L in water in Wuhan, whereas the lowest concentrations of PFASs were observed at Poyang lake. The annual loadings of PFOA, perfluorohexanoic acid (PFHxA), PFBS, perfluorooctane sulfonic acid (PFOS) and the total PFASs in the Yangtze River were 6.8 tons, 2.2 tons, 8.2 tons, 0.88 tons, and 20.7 tons, respectively. Wuhan and Er'zhou of Hubei contributed the most amounts of PFASs into the Yangtze River. A correlation was found between some PFASs, for example PFBS and PFOS, which suggests that both of these PFASs originate from common sources in the region.

1. Introduction

Perfluoroalkyl substances (PFASs) are a class of synthetic fluorinated organic compounds with hydrophobic and oleophobic properties, and they are widely used in consumer and industrial applications such as textiles, clothes, carpet, paper coating, cosmetics, waterproof agents, and firefighting foams (Key et al., 1997; Moody and Field, 2000; Giesy and Kannan, 2001; Lewandowski et al., 2006). Perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) are the two most prevalent groups of PFASs in the environment, and among them

perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the typical PFAS compounds transformed from many other precursors of PFASs such as N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE), and N-ethyl perfluorobutane sulfonamide (EtFBSA) (Martin et al., 2006; Rhoads et al., 2008).

Because of the high energy of the covalent carbon-fluorine bond, PFASs are highly chemically stable and resistant to hydrolysis, photolysis and biodegradation in the environment (Banks et al., 1994). Incomplete removal of PFASs by waste water treatment plants (WWTPs) (Schultz et al., 2006; Sun et al., 2011), and transport by water flow and oceanic currents (Yamashita et al., 2008) and atmosphere (Stock et al., 2007) make them ubiquitously distributed in various environmental media including air (Li et al., 2011b), water (Hansen et al.,

2002; Hong et al., 2013), sediment (Higgins et al., 2005; Benskin et al., 2011), biota (Giesy and Kannan, 2001; Tao et al., 2006), and human (Hansen et al., 2001). They have even been found in some remote areas, such as the Arctic (Benskin et al., 2012) and Tibetan Plateau (Shi et al., 2010). In general, the concentrations of PFOA and PFOS are found in the range from not detected (ND) to hundreds of 144 ng/L in surface water (Hansen et al., 2002; Hong et al., 2013) and ND to 3.76 ng/g levels in sediment (Higgins et al., 2005; Benskin et al., 2011).

PFAS-related manufacturing processes, wastewater discharges, leaching of landfills, precipitation, contaminated runoff and air deposition are thought to be the direct sources for PFASs in the aquatic environment (Ahrens et al., 2009a; Paul et al., 2008; Busch et al., 2010; Cai et al., 2012). Long chain (more than seven fully fluorinated carbon atoms) PFCAs and PFSAs are shown to be bioaccumulative (Martin et al., 2003) and have potential adverse effects on humans and animals (Lau, 2012; Peters and Gonzalez, 2011). In 2000, 3 M announced the phase out of PFOS, and PFOA and their longer chain homologues (Lindstrom et al., 2011). The European Union started to ban the usage of PFOS in consumer products (Directive, 2006/122/EC) and PFOS with its precursor, perfluorooctanesulfonyl fluoride (POSF), were listed to Annex B of the Stockholm Convention in 2009, calling for restricted production and use worldwide (UNEP, 2009).

China is currently one of the biggest PFASs producers in the world (Yu, 2010). Aquatic environments are the main receiver of these PFASs. It is essential to know the contamination profiles of PFASs in the Chinese aquatic environment. The Yangtze River is the longest river in China and the third-longest in the world. It flows more than 6300 km from the Qinghai–Tibet Plateau eastward to the East China Sea at Shanghai (Chen et al., 2001). It is also one of the biggest rivers by discharge volume in the world (average flow: 23 400 m^3/s at Hankou station) (Zhang et al., 2007). The Yangtze drains one-fifth of the land area of China and its river basin is home to one-third of the Chinese population. It served for drinking water source, irrigation, sanitation, transportation and industry. But in recent three decades, this river has been suffered more from industrial pollution, agricultural run-off and siltation. However, little information at the catchment scale is available about PFASs contamination in the Yangtze River in the literature (So et al., 2007; Jin et al., 2009; Lu et al., 2011).

The objective of this study was to investigate the contamination profiles of eighteen PFASs in water and sediment from the Yangtze River in the central and east region of China, and to estimate the total annual mass loadings of the PFASs in the Yangtze River. In addition, chemical composition profiles of PFASs measured in this study can also be used as fingerprints for source identification. The results from this study can help understand the contamination of PFASs in the Yangtze River and assist local governments to better control these chemicals.

2. Materials and methods

2.1. Chemicals and reagents

Eighteen perfluoroalkyl substances were selected as the target compounds, as shown in Table S1 (Supplementary Data). Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFH$_X$A), and perfluorooctane sulfonamide (FOSA) were purchased from J&K Company (China), Acros Organics (Geel, Belgium), Tokyo Chemical Industries (Portland, OR), and Dr. Ehrenstorfer GmbH (Germany), respectively. PFOA and PFOS were purchased from Accustandard (New Haven, USA). Perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFD$_O$DA), and perfluorotetradecanoic acid (PFTeDA), were purchased from Alfa Aesar (Ward Hill, MA USA). Perfluoroundecanoic acid (PFUnDA), perfluorotridecanoic acid (PFTrDA), perfluorobutane sulfonic acid (PFBS), and perfluorohexane sulfonic acid (PFH$_X$S) were from Sigma-aldrich (St. Louis, USA). Perfluorodecane sulfonic acid (PFHpS), perfluorodecane sulfonic acid (PFDS), N-

ethylperfluorooctane sulfonamidoacetic acid (EtFOSAA), and mass-labeled standards MPFH$_X$A ($^{13}C_2$-PFH$_X$A), MPFOA ($^{13}C_4$-PFOA), MPFNA ($^{13}C_5$-PFNA), MPFDA ($^{13}C_2$-PFDA), MPFH$_X$S ($^{18}O_2$-PFH$_X$S), and MPFOS ($^{13}C_4$-PFOS) were purchased from Wellington Laboratories (Guelph, ON, Canada). The purities of all the analytical standards were ≥95%.

HPLC grade methanol was purchased from Merck Corporation (Darmstadt, Germany). Ultrapure water was supplied by a Milli-Q system from Millipore (Watford, UK). Ammonium hydroxide (10%) and acetic acid were bought from Fluka (Steinheim, Germany). LC–MS grade ammonium acetate (>99%) and methyl tert-butyl ether (MTBE) were purchased from CNW (Dusseldorf, Germany). Oasis WAX extraction cartridges (6 mL, 150 mg) used for extraction and purification of the target compounds were from Waters (Milford, MA, USA). Glass fiber filters (GF/F, pore size 0.7 μm) were supplied by Whatman (Maidstone, England). Individual stock solutions of the target analytes and internal standards were prepared in methanol and stored in polypropylene (PP) bottles at −18 °C.

2.2. Sample collection

Surface water and sediment samples were collected in summer and winter of 2013 from 24 sites (C1 to C24) in the Yangtze River, China (Fig. 1). The basic information of each sampling site is presented in Table S2 (Supplementary Data). Surface water samples were collected in clean high density polyethylene (HDPE) bottles, while sediment samples were collected by a stainless grab sampler and then stored in 50 mL PP tubes. The HDPE containers were rinsed with tap water, Milli-Q water, methanol, and water from the particular sampling location prior to use.

The water quality properties of chemical oxygen demand (COD), biochemical oxygen demand (BOD$_5$), total nitrogen (TN), ammonia–nitrogen (NH$_4$–N) and total phosphorus (TP) were performed according to the standard methods (Clesceri et al., 2001). COD was measured using the potassium dichromate method. BOD$_5$ was measured by the 5-day BOD test using the azid modification of the iodo metric method. TN and NH$_4$–N were determined by a UV–vis spectrophotometer (Shimadzu Instrument Co. Ltd., UV-2450, Japan) (APHA, 1998; Shao et al., 2013). Total organic carbon (TOC) was measured by a TOC analyzer (LiquiTOC, Elementar Analysensyteme Co., Germany). The pH and dissolved oxygen (DO) were monitored on line by a pH/DO meter (YSI-Pro2030; YSI Incorporated, Yellow Springs, OH, USA). And the results of water quality parameters are listed in Tables S2 and S3.

The collected sediment samples were stored in a cold room (4 °C) in darkness once arriving at the laboratory, then freeze-dried, homogenized and passed through a 0.83 mm mesh, and finally stored in 4 °C until the extraction.

2.3. Sample preparation and extraction

Three replicate water and sediment samples were extracted for each sampling site. The collected water samples were first filtered using glass fiber filters and extracted within 48 h by solid phase extraction (SPE) using Waters Oasis WAX Cartridges (150 mg, 6 mL), which was adopted from a previous reported method (Taniyasu et al., 2005). Briefly, prior to SPE, each water sample (500 mL each) was fortified with 5 ng (50 μL, 100 μg/L) of an internal standard mixture (MPFH$_X$A, MPFOA, MPFNA, MPFDA, MPFH$_X$S, and MPFOS). After preconditioning of each cartridge with 4 mL of 0.1% NH$_4$OH in methanol, 4 mL of methanol and 4 mL of Milli-Q water, then the water samples were loaded onto the cartridges at approximately one drop per second. The cartridges were then dried under vacuum. Elution was performed using 4 mL of methanol and 4 mL of 0.1% NH$_4$OH in methanol in sequence. Each extract was brought to dryness under a gentle stream of nitrogen and reconstitute in 0.5 mL methanol, and the extract was further filtered through a 0.22 μm nylon filter into a 1 mL PP vial with polyethylene (PE) cap, and stored in −18 °C until the analysis.
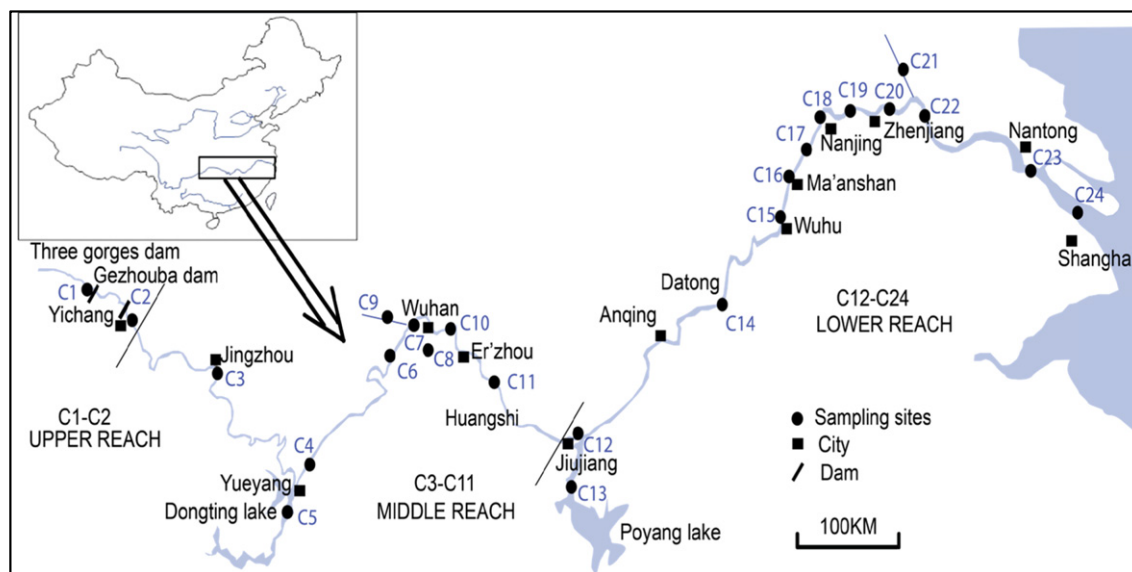
Fig. 1. Map showing the sampling sites in the Yangtze River in 2013.

The freeze-dried sediment samples were extracted using the method described elsewhere (Hansen et al., 2001). Briefly, two grams of homogenized sediment was weighed into a 50 mL PP tube, then 5 ng (50 μL, 100 μg/L) of an internal standard mixture was added to the tube, and the sample was mixed with 2 mL of Milli-Q water by vortexing for 2 min. Then 2 mL of 0.25 M Na_2CO_3 and 1 mL of 0.5 M tetrabutylammonium hydrogen sulfate (TBAHS) solutions were added for extraction by vortexing for 5 min, followed by addition of 5 mL of methyl *tert*-butyl ether (MTBE) and finally the tube was shaken for 20 min. After centrifuging for 25 min at 2259 g, the supernatant was collected from the tube by pipette. Another 5 mL of MTBE was added into the remnant aqueous mixture again, followed by shaking and centrifuging with the above condition, the supernatant was combined with the first one in a 10 mL PP tube. The MTBE extract was brought to dryness under a gentle stream of nitrogen, and reconstituted in 500 μL methanol. The final extract were treated the same as those for the water samples.

2.4. Instrumental analysis and quality control

Quantitative analysis of the target PFASs in the extracts were conducted by high performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) with electrospray ionization (ESI) in the negative mode. An Agilent 1200 HPLC system coupled with an Agilent 6460 triple quadrupole (QQQ) mass spectrometer (Agilent Technologies, Santa Clara, CA) was used for the chemical analysis. Five microliters of aliquot of each extract was injected into a Betasil C18 column (2.1 mm i.d. ×50 mm length, 5 μm; Thermo Hypersil-Keystone, Bellefonte, PA) with a pre-column (2.1 mm, 0.2 μm; Agilent Technologies), with 2 mM ammonium acetate aqueous solution (solvent A) and methanol (solvent B) as the mobile phase at a flow rate of 250 μL/min. The gradient program was given as follows: 10% B at 0 min, then increased to 35% B at 0.1 min, 55% B at 7 min, 95% B at 17 min, and kept the same to 18 min, then decreased to 10% B at 20 min. The capillary was held at 3500 V. Dry and sheath gas flows were kept at 6 and 12 L/min, respectively. Dry and sheath temperatures were kept at 325 °C and 350 °C, respectively. The tandem mass spectrometer was operated under multiple reaction monitoring (MRM) mode, with the MS/MS mass transition ions, fragmentor and collision energy being listed in Table S1.

Strict quality assurance and quality control (QA/QC) were followed during the sampling, extraction and analysis. Field controls and procedural blanks and recoveries were determined for each set of extraction.

To reduce instrumental background contamination arising from HPLC or solvents, a ZORBAX SB-Aq trap column (Agilent technologies, 50 × 4.6 mm, 3.5 μm particle size) was inserted in the water-eluent line, immediately above the solvent-mixing cell. All field and laboratory blanks were found to be less than the limits of quantification (LOQs). The LOQ was defined as 10 times the background signal of solvent blank, while the limit of detection (LOD) was defined as 3 times the background signal of solvent blank. Blanks and control samples were run every 7 samples to check for any carryover, background contamination, precision and accuracy of the recovery. The use of Teflon coated lab ware and glassware were avoided during all steps of sampling, pretreatment and analytical processes to minimize contamination of the samples. PFAS standards, extracts and samples should not come in contact with any glass containers as these analytes can potentially adsorb to glass surfaces.

The matrix recoveries, limit of detection (LOD), and limit of quantification (LOQ) of each PFAS in water and sediment are given in Table S4.

2.5. Mass loading estimation

The total annual mass loadings of PFASs in the Yangtze River per year were calculated based on the following equations:

$$I_{water} = C_{s\,wet} \times Q_{wet} + C_{s\,dry} \times Q_{dry}$$
$$I_{sediment} = C_s \times M_s$$
$$I_{total} = I_{water} + I_{sediment}$$

where I_{water}, $I_{sediment}$ and I_{total} are the annual mass loadings of a chemical in water (dissolved phase), sediment (in surface sediment phase), and total of the Yangtze river, respectively, with the unit of kg; $C_{s\,wet}$ and $C_{s\,dry}$ are aqueous concentrations of PFASs in the wet and dry seasons with the unit of ng/L. Wet season and dry season are 6 months per year. The water flow values of wet season Q_{wet} and dry season Q_{dry} were available on the web of China Hydrology with the unit of m^3/s; considering the effect of tide level, the water run-off value of sampling station C14 (Datong) and PFAS concentrations in sampling station C24 (Shanghai) were applied in this equation. C_s is the median value of PFASs in sediment with the unit of ng/g; Ms is the annual sediment loadings in the Yangtze River, with a reported value of 0.8×10^8 tons/year (Chen et al., 2001).

2.6. Statistical analysis

A Spearman correlation analysis was used to examine possible correlations among various PFASs in the samples, while a linear regression was conducted to evaluate relationships among the contaminants. A one-way ANOVA was performed to determine significant difference between the concentrations of PFASs detected in the Yangtze River and seasonal variations. All statistical analyses were performed with SPSS software (Version 18.0, SPSS Incorporate, Chicago). The significance level was set at $p = 0.05$.

3. Results and discussion

3.1. Concentrations and composition of PFASs in surface water

The concentrations of eighteen individual PFASs in surface water of Yangtze River are shown in Fig. 2. The total concentrations of the PFASs in the water phase of Yangtze River ranged from 2.20 to 74.56 ng/L in summer, and 3.62 to 69.0 ng/L in winter (Table 1). The PFASs with fluorinated carbon atoms equal or less eight (C4–C8: PFOS, PFOA, PFBA, PFPeA, PFBS, PFHxA and PFHpA) exhibited higher detection frequencies (66.7–100%) than those PFASs with fluorinated carbon atoms more than eight (C9–C14: PFUnDA, PFDoDA, PFTrDA, PFTeDA and PFDS), with their detection frequencies of 0–4.2%, and concentrations at most sampling sites being less than their LODs. Among the 18 target PFASs, three PFCAs: PFBA, PFHxA and PFOA were the most frequently detected compounds with 100% detection frequencies, followed by PFPeA and PFBS with their detection frequencies of 91.7%. In the Yangtze River, PFOA and PFBS were the predominant PFAS compounds in the water, with relatively high concentrations and detection frequencies (Table 1).

The highest concentrations of PFASs (74.6 ng/L in summer, and 69 ng/L in winter) were measured at the site C8, where PFBS was the predominant compound. It should be noted that the site C8 was situated in an inner lake Donghu in the city Wuhan, which is one of the most important production bases of the fluorochemical industry in China (Zhou et al., 2013). The concentrations of PFASs at this site were about twenty fold higher than those at the site C13 (Poyang lake), where the lowest concentration of PFASs of 3.62 ng/L was observed. Poyang Lake is located in a less developed region with less population and industrial activities.

The average total concentrations of PFASs (PFASs) in the main stream of Yangtze River were at a range of 13.95–31.91 ng/L, showing limited variations. The PFOA concentrations in the upper and middle reaches (C1–C11; 9.9–15.61 ng/L) were obviously higher than those in the lower reach (C12–C24; 6.81–8.24 ng/L), which indicates no significant input sources of PFOA along the studied section of Yangtze River. The lower concentrations of PFOA in the lower reach could be explained by the dilution by larger water flows (Table S2). The concentrations of PFBA, PFBS and PFOS in the upper and middle reaches of the Yangtze River were found to be significantly lower than those in the lower reach ($p < 0.05$), indicating the input from PFAS-related industrial wastewater from cities like Wuhan. PFBS increased sharply from 1.14 to 14.53 ng/L from C7 to C11 passing through Wuhan and Er'zhou, most likely due to the global phase-out of PFOS (Weppner and 3M Company, 2000) and the use of PFBS as a substitute for PFOS in this region. Meanwhile, PFBA and PFOS increased from 0.98 ng/L to 2.22 ng/L, and 0.23 to 1.00 ng/L from C7 to C11 after passing through Wuhan and Er'zhou, respectively.

The profiles of relative concentrations of 18 individual PFASs in surface water for summer and winter are displayed in Fig. S1. No obvious difference in the patterns for the summer and winter was observed, but big differences in the contributions of each PFAS to the total PFASs among the sampling sites were found, possibly indicating different PFAS usages in the catchment. The average biggest contributions were PFOA (11.28–87.08%) and PFBS (0.32–50.47%), followed by other PFASs with shorter chains such as PFBA, PFPeA, PFHxA and PFHpA. In addition, much less or no contributions were found from those PFASs with long chain (PFUnDA, PFDoDA, PFTrDA, PFTeDA, FOSA, EtFOSAA and PFDS), which will not be discussed further in this study. Statistical analysis showed that PFOA, PFHxA, PFBS, PFOS and PFBA were found to be related to TN ($p < 0.05$) (Table S5). This suggests that the contamination levels of these PFASs in water might have connection with nitrogen contaminated wastewater discharges into the Yangtze River.

Some previous studies have also reported the occurrence of PFASs, especially PFOA and PFOS in river water globally (Hansen et al., 2002; Mclachlan et al., 2007; Murakami et al., 2008; Yeung et al., 2009; Nakayama et al., 2010; Hong et al., 2013; Wang et al., 2013; Zhang et al., 2013). In general, the PFAS concentrations in the Yangtze River were lower than those in other rivers in the world. This could be explained by the large water flow in the Yangtze River which had dilution effects on concentration levels of PFASs. Several previous studies reported the occurrence of PFASs in water samples collected from different sections of the Yangtze River in 2003, 2006, and 2008, respectively (So et al., 2007; Jin et al., 2009; Lu et al., 2011). Compared with the previous data, the PFOA concentrations in the present study were higher in the upper and middle reaches of the Yangtze River (median values: 4.3 ng/L in 2004, and 5.4 ng/L in 2003), but lower in the estuary of Shanghai (median value: 34 ng/L in 2004; and mean value: 115.5 ng/L in 2008). The PFOS concentrations in 2013 (median value: 0.65 ng/L) exhibited a big decrease when compared to those in 2003(median value: 4.7 ng/L), while the PFBS concentrations in 2013 (median value: 3.9 ng/L) were much higher than those in 2004 (median value: 0.97 ng/L). This finding indicates that the PFBS has increasingly been used as a substitute of PFOS in PFOS-related products.
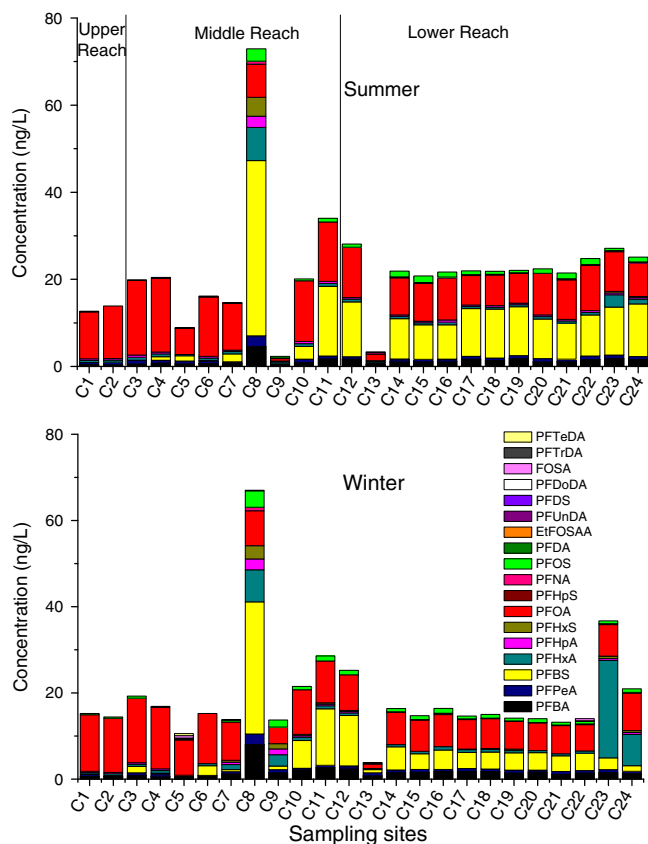

Fig. 2. Concentrations of PFASs in surface water of the Yangtze River in the two seasons. C1–C24 represent the sampling sites.

Table 1
Range, mean, median concentrations and detection frequency of PFASs in water (ng/L) and sediment (ng/g dw) of two seasons in the Yangtze River.

Matrice			PFBA	PFPeA	PFBS	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFDA	PFUnDA	PFDS	FOSA	PFASs
Water	Summer	Range	0.35–4.68	n.d[a]–2.59	n.d–41.9	0.26–7.91	n.d–2.61	n.d–4.50	0.52–18.0	n.d–0.70	n.d–3.06	n.d	n.d–0.10	n.d	n.d	2.20–74.6
		Mean	1.25	0.64	7.68	0.94	0.45	0.20	9.55	0.19	0.70	n.d	0.01	n.d	n.d	21.6
		Median	1.12	0.60	7.99	0.56	0.38	n.d	9.34	0.19	0.63	n.d	n.d	n.d	n.d	21.0
		D.F[b]	100%	95.8%	83.3%	100%	95.8%	12.5%	100%	79.2%	70.8%	0%	0%	0%	0%	
	Winter	Range	0.45–8.38	n.d–2.51	0.09–32.0	0.11–22.7	n.d–2.59	n.d–3.27	1.02–15.8	n.d–0.86	n.d–3.93	n.d–0.33	n.d	n.d–0.21	n.d–0.62	3.62–69.0
		Mean	1.67	0.57	4.56	2.13	0.32	0.31	8.44	0.11	0.79	0.02	n.d	0.01	0.05	18.98
		Median	1.45	0.54	3.69	0.58	0.12	0.06	7.78	0.07	0.66	n.d	n.d	n.d	n.d	15.17
		D.F	100%	87.5%	100%	100%	50%	50%	100%	54.2%	91.7%	8.3%	0%	8.3%	12.5%	
Sediment	Summer	Range	n.d	n.d	n.d–0.13	n.d–0.32	n.d	n.d	0.07–0.55	n.d–0.06	n.d–0.59	n.d–0.06	n.d–0.10	n.d–0.06	n.d	0.13–1.44
		Mean	n.d	n.d	0.01	0.07	n.d	n.d	0.24	0.01	0.06	0.01	0.01	n.d	n.d	0.46
		Median	n.d	n.d	n.d	0.03	n.d	n.d	0.24	n.d	n.d	n.d	n.d	n.d	n.d	0.39
		D.F	0%	0%	4.2%	87.5%	0%	0%	100%	4.2%	45.8%	4.2%	16.7%	0%	0%	
	Winter	Range	n.d	n.d–0.04	n.d–0.20	n.d–0.05	n.d	n.d	0.03–0.72	n.d	n.d–0.51	n.d–0.03	n.d	n.d–0.03	n.d	0.05–1.40
		Mean	n.d	0.01	0.01	0.01	n.d	n.d	0.24	n.d	0.06	n.d	n.d	0.01	n.d	0.33
		Median	n.d	n.d	n.d	0.01	n.d	n.d	0.26	n.d	0.01	n.d	n.d	n.d	n.d	0.29
		D.F	0%	16.7%	4.2%	54.2%	0%	0%	100%	0	50%	0%	0%	20.8%	0%	

Note: For those not detected PFASs at any site in water and sediment were not presented in this table.
[a] n.d: not detected;
[b] D.F: detection frequency.

3.2. Concentrations and compositions of PFASs in sediment

Among the 18 target compounds, seven PFCAs (PFPeA, PFHxA, PFOA, PFNA, PFDA and PFUnDA) and three PFSAs (PFBS, PFOS and PFDS) were detected in the sediments of Yangtze River. Unlike the contamination of PFASs in surface water, the concentrations of PFASs in the sediments of Yangtze River were very low, and most PFASs were not detected at the majority of sampling sites (Fig. 3). The total concentrations of PFASs in the sediments from Yangtze River ranged between 0.05 and 1.44 ng/g dry weight (dw). PFOA and PFOS were the predominant PFAS compounds found in the Yangtze River (Table 1).

As shown in Table 2, the most frequently detected three compounds were PFOA, PFHxA, and PFOS, with their detection frequencies of 100%, 70.8%, and 47.9%, and mean concentrations of 0.24 ng/g, 0.04 ng/g and 0.06 ng/g, respectively. The other less frequently detected compounds were PFUnDA, PFPeA, PFBS, PFNA and PFDA, with their detection frequencies of below 10%. The other PFASs, including PFBA, PFHpA, PFDoDA, PFTrDA, PFTeDA, PFHxS, PFHpS, EtFOSAA and FOSA, were not detected in the sediments of any sites. The different occurrence patterns for the PFASs were most possibly related to their usages and physico-chemical properties (Li et al., 2011a).

By comparison, the sediment phase showed different composition profiles of PFASs to the water phase. Among the 18 target PFASs, PFOA was still the dominant PFAS contaminant detected in the sediment phase of most sites of the Yangtze River, followed by PFHxA and PFOS. PFOA contributed 30.45%–91.24% of the total PFASs, while PFHxA, and PFOS contributed 1.68–26.54% and 0–65.07%, respectively.

Similar to the spatial distribution tendency of PFASs in surface water, relatively higher PFASs were found at the site C8, with the highest PFAS concentration up to 1.35 ng/g. Due to the partition process, the long chain PFASs (PFNA, PFDA, PFUnDA, PFOS and PFDS) were more frequently detected in the sediment phase than in the water phase. Different composition profiles observed between water and sediment phases indicated that the distribution of individual PFAS was closely dependent on its physicochemical characteristics such as solubility. The solubilities of PFASs differ from compound to compound, with the short chain PFASs have high solubility and long chain ones have low solubility; for example, the solubility for PFBS is 51 000 mg/L and PFOS 670 mg/L (Lau et al., 2007). The PFASs with long carbon chain would be more prone to partition onto the sediment phase.

The profiles of relative contributions of 18 individual PFASs in the sediment of Yangtze River for summer and winter are displayed in Fig. S2. No obvious seasonal difference in the PFASs patterns was observed. The average largest contributions were from PFOA (28.72–91.24%) and PFOS (0–65.07%), followed by other PFASs with shorter chains such as PFHxA and PFHpA; but much less or no contributions were found from those PFASs with long chain (PFUnDA, PFDoDA, PFTrDA, PFTeDA, FOSA, EtFOSAA and PFDS).

In the sediment of the Yangtze River, the concentration levels of PFOS, PFOA and PFASs were found to be correlated with TOC, TP, TN and NH_4–N ($p < 0.05$) (Table S5). Sediment properties can play an important role in the distribution of organic compounds in riverine environment, but the influential processes or mechanisms are very complicated and varied from compound to compound. Perfluorocarbon chain length is the dominant structural feature influencing their partitioning onto sediment (Labadie and Chevreuil, 2011). Partitioning of PFASs onto sediment has been found strongly correlated with sediment TOC (Ahrens et al., 2009b; Higgins and Luthy, 2006). Higgins and Luthy (2006) also found that electrostatic interactions could play a role in sorption of PFASs to sediment.

3.3. Seasonal variations in the Yangtze River

After screening the PFASs in the Yangtze River of China, no clear seasonal pattern was found concerning their levels in surface water and sediment. In general, no obvious significant differences between the
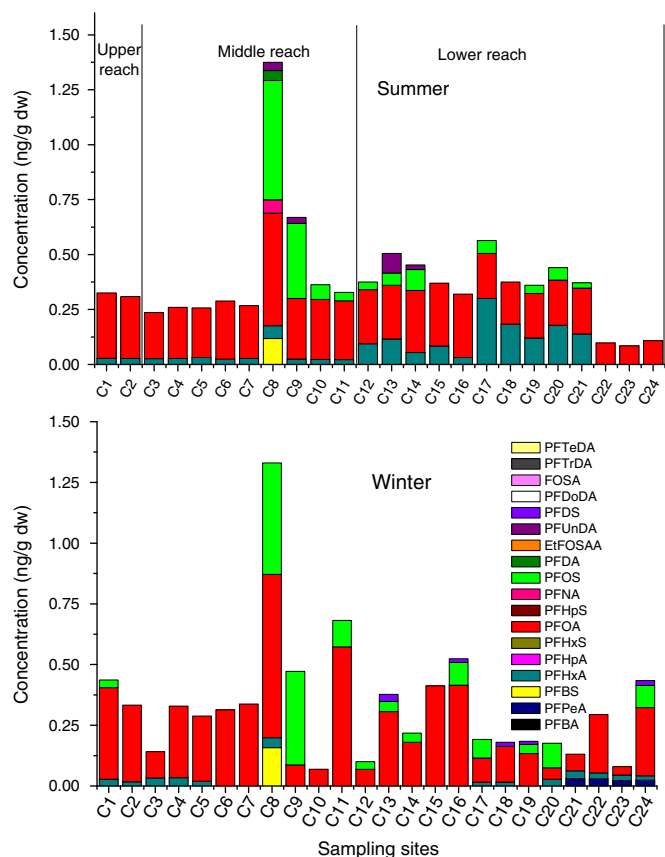
Fig. 3. Concentrations of PFASs in sediment of the Yangtze River in the two seasons. C1–C24 represent the sampling sites.

Table 2
Estimated annual loadings (tons) of PFASs discharged to the Yangtze River.

Compounds[a]	I_w	I_s	I_{total}
PFBA	1.36	–	1.36
PFPeA	0.509	–	0.509
PFBS	8.17	–	8.17
PFHxA	2.21	0.0022	2.21
PFHpA	0.325	–	0.325
PFHxS	0.258	–	0.258
PFOA	6.81	0.017	6.83
PFNA	0.191	–	0.191
PFOS	0.886	0.00192	0.888
PFASs	20.7	0.0242	20.7

[a] Other PFASs are not listed in this table as they were not detected both in water and sediment.

summer and winter were found for majority PFASs in the surface water and sediment of Yangtze River ($p > 0.05$). However, some PFASs, such as PFBA and PFBS had obvious seasonal variations (Table 1).

No obvious seasonal variations in PFAS concentrations were observed in the influents of WWTPs in USA (Loganathan et al., 2007), but contradictory results were found in the WWTPs from Singapore, with the PFOS and PFOA concentrations in the dry season higher than in the wet season (Yu et al., 2009). Seasonal variations in PFAS concentrations in water could be affected by many factors, such as the water flows, water quality properties, weather, and PFASs usage and discharge in the catchment. Considering the concentrations of PFASs in the Yangtze River in the two seasons were almost at the same level, but the water flow in the wet season is nearly four times higher than in the dry season, the mass loadings of PFASs discharged to Yangtze River would be much higher in summer. One possible contribution source is from the runoff in rainy days (nonpoint source pollution) which might carry PFASs (Yu et al., 2009).

3.4. Pollution loading of PFASs in the Yangtze River

PFASs in the Yangtze River could be originated from various sources. Sources could include the waste water discharge from industries and WWTPs, whereas landfill leachate, dry or wet atmospheric deposition, and soil/street surface runoff have also been suggested as non-point sources (Ahrens et al., 2009a; Paul et al., 2008; Busch et al., 2010; Cai et al., 2012). PFAS levels and profiles in the Yangtze River provided some important insights. A Spearman rank correlation analysis was performed among the individual PFASs in water samples from Yangtze River for source determination (Table S6). Significant positive associations ($p < 0.05$) were observed among part of the PFASs in water samples from Yangtze River. Positive correlations between PFASs suggested the

presence of common contamination sources in the Yangtze River. PFCAs and PFOS might have different contamination sources as no significant associations were found among these compounds. PFBA and PFBS were strongly correlated with each other ($r = 0.936$, $p < 0.0001$), suggested the possibility of a common pollution source for these compounds. However, no significant correlation was found between other PFASs, such as PFOA with PFOS, the most widely used PFASs; therefore, PFOA and PFOS could be originating from different contamination sources. So et al. (2004) showed that PFOS was significantly correlated with other compounds including FOSA, PFNA and PFHpA in water samples of Yangtze River and Pearl River.

Based on the concentration data from the two sites (C6 and C11), it is estimated that the cities Wuhan and Er'zhou of Hubei province discharged 11.6 tons of PFASs into the Yangtze River, of which PFBS contributed 10.1 tons, followed by the PFBA (0.864 tons). This suggests widespread use of PFASs in industrial applications in these two cities. There are dozens of major industries, including fluorochemical, food processing, textiles, insecticides, pharmaceutical, and electroplating located in Wuhan (Zhou et al., 2013; Wang et al., 2013), which could be the potential pollution sources. Wang et al. (2013) reported PFASs contamination in the effluents of a manufacturing plant in Wuhan, being responsible for the high PFAS concentration in the surrounding river water. High concentrations of PFASs, especially thousands ng/L of PFBA (max concentration 47 800 ng/L) and PFBS (max concentration 15 300 ng/L), were observed in surface water near a fluorochemical plant in Wuhan (Zhou et al., 2013). This is in agreement with the sharp increase of PFBS and PFBA in Wuhan section in the present study. Another important source for PFASs might be WWTPs. Previous studies reported that the conventional treatment could not remove PFASs efficiently, which results in discharge of PFASs in the effluents (Loganathan et al., 2007; Sun et al., 2011). High concentrations of PFASs (dozens to hundreds of ng/L) have been reported in the Wuhan WWTP effluents (Sun et al., 2011; Kim et al., 2012).

Another major pollution source for PFASs along the Yangtze River is located between the sites C22 and C23 in Nantong, which discharged approximately 6 tons of PFHxA, accounting 98.6% of the total PFASs. Other PFASs had no obvious input sources between these two sites.

3.5. Estimated annual mass loadings of PFASs in the Yangtze River

According to the mass loading calculation equations, the annual mass loadings of PFASs via water discharged to the East China Sea and the particulates sorbed onto sediment are presented in Table 2. It is obvious that the mass loading of PFASs primarily exist in the water (dissolved) phase. The mass of PFASs in dissolved phase (water phase) accounted for more than 99% of the total PFASs. The calculated annual loadings of PFOA, PFHxA, PFBS, PFOS and the total PFASs in the Yangtze River were 6.8 tons, 2.2 tons, 8.2 tons, 0.88 tons, and 20.7 tons, respectively. These values were a little higher than the previous estimated annual loadings (PFOA, 3.780 tons; PFOS, 0.534 tons; PFNA, 0.237 tons) from the Yangtze river to the East China Sea (Yeung et al., 2009),

suggesting the increasing usage of PFASs in the Yangtze river basin in the last decade. Although the PFAS concentrations in the Yangtze River (maximum concentration for PFOA and PFOS were 18 ng/L and 3.93 ng/L, respectively) are much lower than those in the majority rivers in the world (e.g. the PFOA and PFOS concentrations in Tamagawa were 107 ng/L and 143 ng/L; tens to hundreds of ng/L for individual PFAS in Mississippi river) (Yeung et al., 2009; Nakayama et al., 2010), the mass loading of PFASs in the Yangtze River are still higher than those in other rivers due to its huge annual water flow (annual mass loading of PFOA and PFOA in Tamagawa were 0.045 tons and 0.060 tons) (Yeung et al., 2009). But the mass loading of PFASs was slightly lower than the European rivers, with the annual mass loading of PFHxA, PFHpA, PFOA and PFNA being 2.8 tons, 0.86 tons, 14.3 tons and 0.26 tons (McLachlan et al., 2007), and much lower than that in the Mississippi River with higher PFAS concentrations (Nakayama et al., 2010). Considering their persistence and bioaccumulation properties, the PFASs in the Yangtze River would be transported to the East China Sea, and finally into the ocean. This could have significant environmental implications, such as their significant mass contribution, global exchange between the ocean and atmosphere, accumulation in biota, and negative impacts on the global ecosystem.

4. Conclusions

Screening of 18 PFASs in surface water and sediment from the Yangtze River showed that PFOA was the predominant compound, followed by PFBS. With comparison to the previous monitoring data, a decrease in the PFOS concentrations and an increase in the PFBS concentrations in the river basin were found. This suggests that PFBS as a substitute of PFOS is increasingly manufactured and discharged to the receiving aquatic environment due to the global phase-out of PFOS-related products. It was also found that the river section between Wuhan and Er'zhou of Hubei province received the most discharge of PFASs from various PFAS-related industries in the two cities. Although the contamination levels of PFASs in the Yangtze River were relatively low, the annual mass loadings to the East China Sea were very large due to its high water flow. Therefore, proper measures should be taken to control industrial wastewater discharge into the river system in order to reduce the potential human and ecological risks from the PFASs. Further research should explore source contributions of PFASs along the Yangtze River.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.06.033.

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