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Occurrence and trends in concentrations of perfluoroalkyl substances (PFASs) in surface waters of eastern China

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Abstract

Spatial distributions of perfluoroalkyl substances (PFASs) were investigated in surface waters in eastern China in 2011, covering Shanghai, Jiangsu and Zhejiang Province. A total of 39 samples of surface waters, including 29 rivers, 6 lakes and 4 reservoirs were collected. High performance liquid chromatography/negative electrospray ionization-tandem mass spectrometry (HPLC/(-)ESI-MS/MS) was analyzed for seventeen PFASs. PFAS pollution was greater in Shanghai than that in Zhejiang Province. Concentrations of the sum of PFASs in Shanghai and Kunshan ranged from 39 ng/L to 210 ng/L, while in Zhejiang Province, the sum of concentrations of PFASs ranged from 0.68 ng/L to 150 ng/L. Perfluorooctanoic acid (PFOA) was the most prevalent compound in Shanghai. In contrast, PFOA and perfluorohexanoic acid (PFHxA) were the most prevalent compounds in Zhejiang Province. Concentrations of perfluorooctane sulfonate (PFOS) ranged from <0.07 to 9.7 ng/L. Mass flows of rivers that would flow into the East China Sea were calculated, and it was determined that more than 4000 kg PFASs are discharged into the East China Sea every year. Correlation analyses between concentrations of individual PFASs were conducted and the results showed that correlation between PFHxA and PFOA was positive, while the correlation between PFHxA and perfluorooctane sulfonamide (FOSA) was negative in Shanghai, which indicated that PFHxA and PFOA have common sources. Results of principal component analysis (PCA) of individual PFASs profiles showed that PFHxA and FOSA owned high factor loadings in different principal components.

Keywords:

PFASs, surface waters, the eastern China, spatial distribution, mass flow, Asia

1. Introduction

Because of their characters of great surface activity, chemical stability and hydrophobic and oleophobic amphiphylic nature, perfluoroalkyl substances (PFASs) have been widely used in various processes and products, including production of emulsifiers, surfactants, dust preventive, disposable tableware additives, and fire-fighting foams during the last half century (Giesy and Kannan, 2002; Olsen et al., 2005; Prevedouros et al., 2006; Olsen et al., 2007; Giesy et al., 2010). Previous studies have documented that widespread application as well as environmental persistence and bioaccumulation of terminal degradation products of PFAS precursors have resulted in global occurrence of PFASs in atmosphere (Kim et al., 2012), waters (Zushi and Masunaga, 2011), sediments (Naile et al., 2013), not only from urban cities but from remote areas such as Qinghai-Tibet Plateau (Shi et al., 2010), polar regions (Cai et al., 2012a,b), etc. Overall, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were the two most observed and reported PFASs because of their abundant production and wide use in fluoropolymer manufacture (Prevedouros et al., 2006).

In 2009, PFOS and its related compounds were listed in Annex B of the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) (Wang et al., 2009). In more developed countries, policies and regulations have reduced production of PFOS and PFOA. In response to the US EPA 2010/2015 PFOA Stewardship Program, the working direction of developed countries is elimination of PFOA and related chemicals from emissions and products before 2015 (U.S. EPA 2009). Since the international macro-control of eight-carbon PFASs was introduced, applications of PFOS and PFOA have been restricted. Shorter-chain PFASs (carbon chain length less than seven), which have lesser toxic potency than the 8-carbon PFASs (Buhrke et al., 2013), have been increasingly used after the voluntary phase-out of perfluorooctanesulfonyl fluoride (POSF) by the 3M Company in 2000 (Olsen et al., 2005). In Japan, PFNA has become the most prevalent PFASs in the Tokyo Bay basin (Zushi et al., 2011), PFBS and perfluorobutanoic acid (PFBA) dominated PFASs in the River Rhine (Möller et al., 2010), while PFBS was the most prevalent PFASs in the Netherlands (Kwadijk et al., 2010) and Fuxin in China (Bao et al., 2011). In China, concentrations of some shorter-chain substitutes are increasing in surface waters from various industrial areas, such as perfluorohexanoic acid (PFHxA) in Liaoning Province (Sun et al., 2011) and in Taihu Lake in Jiangsu Province (Yu et al., 2013), whereas in Hubei Province PFBS and PFBA were the predominant PFASs (Zhou et al., 2013). Current contaminations of PFASs mainly arise from application of alternatives and consumption of stockpiles of longer-chain PFASs. Monitoring and control of shorter-chain PFASs in the future is needed.

Over the last decades development of China’s national economy has made remarkable achievements with rapid growth of industry and swift increase of gross domestic product (GDP), and it has become one of the world’s greatest economic entities. The Yangtze River delta, one of the most investigated areas, is in a unique position in the study of PFASs because it is located at the junction of eastern coastal developed areas, involving Shanghai and parts of Jiangsu and Zhejiang Provinces, which is known as the first economic zone and one of the major fluoropolymer manufacturing bases of China. Shanghai, a greatly industrialized, densely populated and prosperous city, is situated where the Huangpu River receives effluents containing PFASs. To date, investigations of PFASs in surface waters of cities around the Yangtze River delta (Pan and You, 2010; So et al., 2007) have focused primarily on PFOA and PFOS, and further comprehensive studies about variation of dominant PFASs and restructure of PFAS patterns are required.

In the present study, concentrations of 17 PFASs were quantified in 39 surface waters, which were collected in eastern China, including 28 rivers, 7 lakes and 4 reservoirs. The objectives of this study were to: (1) determine concentrations, profiles, patterns of relative concentrations and spatial distributions of PFASs in eastern China; (2) identify possible pollution sources in eastern China; (3) calculate discharge loads of PFASs to the East China Sea.

2. Materials and methods

2.1 Sampling

Samples of surface water were collected from three areas (Shanghai, Jiangsu Province and Zhejiang Province) of eastern China from May to July, 2011, involving the major rivers, lakes and reservoirs that widely distributed over the investigated areas. Details regarding the sampling date, sampling location and area description about the investigated areas can be found in Table S1. For simplicity, all the sampling sites located in Zhejiang Province are abbreviated as ZJ1-ZJ29, all the sampling sites located in Shanghai are abbreviated as SH1-SH8, and all the sampling sites located in Kunshan, Jiangsu Province are abbreviated as KS1-KS2 (Figure 1). Additionally, for convenience, samples were divided into two zones, an industrial zone: SH1-SH2 and KS1-KS2; and a comprehensive zone: ZJ1-ZJ29.

2.2 Chemicals and standards

Seventeen PFASs, including perfluoroalkane sulfonates (PFSAs) (C_4, C_6-C_8, and C_{10}), perfluoroalkyl carboxylates (PFCAs) (C_4-C_{14}), FOSA were quantified. Nine mass-labeled PFSAs were used as the internal standard (IS) mixture, i.e., ^{13}C-labeled ionic PFSAs and ^{18}O-labeled perfluorohexane sulfonate (PFHxS). 2H-perfluoro-[1,2-$^{13}C_2$]-2-decenoic acid (8:2 FTUCA) was used as the injection standard (InjS). Methanol (SupraSolv) and ammonium hydroxide (25%, Suparpur) were purchased from Merck (Darmstadt, Germany). The methanol was distilled in a glass apparatus before use, and the Milli-Q water was pre-cleaned through cartridges to remove any residual PFASs in the water.

2.3 Extraction and analysis

1L filtrates filtered by 0.45μm GF/C were solid-phase extracted (SPE) using glass funnels and SPE cartridges (Waters Oasis WAX, 150 mg, 6 cm^3, 30 mm). After being spiked with 1 ng IS (50 pg μL^{-1}, 20 μL), the filtrate was loaded onto the cartridge at a rate of 2 drops per second. The cartridge was then washed with 10 mL Milli-Q water to remove the salt and dried by a vacuum pump to achieve a better recovery. The dried cartridges were eluted using 10 mL methanol with 0.1% ammonium hydroxide. Elutes were reduced to 150 μL under a gentle stream of nitrogen (>99.999%). Before being injected into the instrument, 1 ng (50 μL, 20 pg μL^{-1}) of mass-labeled 8:2 FTUCA as the InjS was spiked into the vials.

Instrumental analyses were performed using a high-performance liquid chromatography-negative electrospray ionization-tandem mass spectrometry system (HPLC/(-)ESI–MS/MS) with a HP 1100 HPLC system (Agilent, Germany) coupled to an API 3000 triple-quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX). The instrumental setup is described elsewhere (Ahrens et al., 2009a).

2.4 Quality assurance and quality control

The method detection limit (MDL), recovery of each spiked sample, field blank and duplicate samples were measured (Table S2). Breakthrough of PFASs was tested by using tandem Oasis WAX cartridges to extract 1 L seawater spiked with 400 pg internal standards. PFASs in the upper cartridge accounted for more than 80% of the sum determined from both cartridges. However, there were no internal standards detectable in the lower cartridge, indicting little breakthrough for PFASs with Oasis WAX cartridge. The MDLs were determined by spiking with 400 pg internal standards in 1 L Millipore water which is pre-cleaned with Oasis WAX cartridge. The MDLs were established at a signal-to-noise (S/N) of 10, which ranged from 0.02 ng L^{-1} (for both PFDA and perfluoroundecanoic acid (PFUnDA)) to 0.14 ng L^{-1} for PFBA. Overall recoveries ranged from 51±21% for $[^{13}C_4]$-PFOS to 78±20% for $[^{18}O_2]$-PFHxS (Table S2). Concentrations were corrected for recoveries of IS in every sample.

3. Results and discussion

3.1 Spatial distributions and compositions of PFASs in eastern China

Concentrations of the 14 PFASs that were detected at concentrations greater than the MDLs are given (Table S3-S4). Only PFOA and PFHxA were detected in all the samples, while perfluorododecanoic acid (PFDoDA) was detected in only two samples and concentrations of perfluorodecane sulfonate (PFDS), perfluorotridecanoic acid (PFTrDA) and perfluorotetradecanoic acid (PFTeDA) were below the MDLs. Here, the discussion focuses on only the 13 PFASs, including C4, C6-C8 PFSAs, C4-C11 PFCAs and FOSA.

Concentrations of sum-PFASs in Shanghai and Kunshan ranged from 39 ng/L to 210 ng/L (Table S4), comparable with those in Shenyang (Sun et al., 2011), less than those from Wuhan (Wang et al., 2013) and Fuxin, Liaoning (Bao et al., 2011), but greater than those for Vietnam (Kim et al., 2013) and Tokyo bay, Japan (Zushi et al., 2011) (Table 1, S5). In Zhejiang Province, concentrations of sum-PFASs were a less with a mean of 43 ng/L and a range of 0.68-150 ng/L, which were also less than those for Singapore (Nguyen et al., 2011), comparable with Liao River

(Yang et al., 2011), but greater than those observed in Seoul and Busan, Korea (Kim et al., 2011) and Huaihe River (Yu et al., 2013) (Table 1, S5). ZJ16 and ZJ17 were collected directly from municipal, sewage outfalls at the inner and outer sluice gate and were considered as spot sources, so they were not included in the calculation of the mean and range of Zhejiang Province.

Patterns of relative concentrations of PFASs varied among locations, which indicate different potential sources between Zhejiang and Shanghai. PFOA was the most prevalent compound in Shanghai and Kunshan accounting for 51% to 86%, while PFOA and PFHxA predominated the concentrations of sum-PFASs in most industrial locations of Zhejiang Province, percentages of which were as great as 80% and 46%, respectively (Figure 2). From results of Principal component analysis (PCA) (Figure 3), two components were extracted from the composition data from Zhejiang Province, Shanghai and Kunshan (n=39), which accounted for 58% and 14%, respectively. PFHxA has high positive correlation with the second principal component (PC2). Samples from some locations in Zhejiang Province (ZJ1-7, ZJ9, ZJ16-17) formed cluster 1, which has high factor loading in PC2. This indicates these samples were more related with PFHxA.

3.2 Sources of PFASs in Zhejiang Province

In Zhejiang Province, four reservoirs (ZJ13, ZJ18-19 and ZJ28), five lakes (ZJ1-2, ZJ10-11 and ZJ20) and twenty river samples (others from ZJ1-ZJ29) were investigated. The greatest concentration of the sum-PFASs was 150 ng/L, found in the West Lake (ZJ1) in Hangzhou (Table S3), even greater than those river samples. There is no known discharges because of the protection around the West Lake. However, due to rapid development of tourism, water consumption of the West Lake scenic area, especially during the wet season when samples were taken, is more than the capacity of the sewage system, wastewater can spill out of sanitary sewers and flow into the West Lake. Diffuse sources such as runoff are also an important potential source (Ahrens, 2011). These can result in contamination of the West Lake with PFASs.

PFOA, PFHxA and PFBS were the most detected compounds in Zhejiang Province. According to the composition profiles, locations ZJ1-ZJ11 were predominated by PFOA and PFHxA, while from ZJ12 to ZJ29 PFOA was the dominant compound, followed by PFHxA and PFBS. Concentrations of PFOS were less with a range from <0.07 to 5.0 ng/L. The results of this study are different from those of previous studies where PFOA and PFOS were the two predominant PFASs (Yu et al., 2013; Thompson et al., 2011; Naile et al., 2010). The greatest concentration of PFOA of 29 samples in Zhejiang Province was 200 ng/L found in ZJ17, which is outside the Cao’e River sluice. However, when river water flowed inside the sluice (ZJ16), the concentration of PFOA was only 90 ng/L, with other individual PFASs changing slightly. This result indicates a point source of PFOA in the vicinity of location ZJ17. The highest concentration of PFHxA observed in the present was 53 ng/L, which was greater than those measured in Liaoning (Sun et al., 2011) and Hong Kong (Loi et al., 2013) in China, Canada (de Solla et al., 2012) and France (Labadie and Chevreuil, 2011) (Table 1, S5). There were unexpected great concentrations of PFHxA in Zhejiang Province, especially for ZJ1-ZJ9, which located in West Lake (53 ng/L), Jiaxing (25-41 ng/L) and Huzhou cities (9.4-30 ng/L) (Table S3). Previous studies also reported that PFHxA was a major compound (Sun et al., 2011; Li et al., 2011) or was of great concentration (Yu et al., 2013; Meyer et al., 2011; Labadie and Chevreuil, 2011). The prevalence of PFHxA instead of PFOS suggests a transformation in manufacture and production of PFASs after restrictions for PFOS and PFOA were introduced, so that PFHxA has become a replacement for C8 compounds (Yu et al., 2013; Meyer et al., 2011). Zhejiang Province is the largest fluoride production base in China (http://www.ewwk.com/NewsView.asp?ID=56), and the Juhua conglomerate as its leading enterprise, that has developed a new C6-based water and oil repellent furnishing without the need for C8 compounds. Usage of C6-based compounds in manufacture industry (Yu et al., 2013) is likely responsible for the greater concentrations of PFHxA observed in this study.

Locations ZJ10 and ZJ11 are located in the inlets southwest of Taihu Lake, which is the third largest freshwater lake in China. Previous studies of Taihu Lake (Table 1) indicate that concentrations of PFASs have varied as a function of time (Yu et al., 2013; Yang et al., 2011; Qiu et al., 2010). Overall, from 2009 to 2011, concentrations of total PFASs, PFCAs and PFSAs have decreased, as well as those individual longer-chain PFASs such as perfluoroheptanoic acid (PFHpA), PFOA, PFNA and PFDA. Concentrations of PFOS (2.0-2.8 ng/L) in our study were lower than that detected in 2009 (3.5-9.4) (Qiu et al., 2010) in the same location. This can be attributed to voluntary phasing-out of PFOS and its related compounds (Cai et al., 2012b). Combined with the contemporaneous study in 2011(Yu et al., 2013), PFHxA is becoming the predominant PFASs in the Taihu lake. This indicated C6-based compounds might be used as substitutes for C8 PFASs in Zhejiang Province.

3.3 Sources of PFASs in Shanghai and Kunshan

Locations SH1-Sh8 were from the Huangpu River in Shanghai, which is the largest river in Shanghai and is responsible for more than 80% directly sewage discharges involving a large part of industrial wastewater (URL 1). Concentrations of PFASs from Shanghai and Kushan (KS1-KS2) were shown in Table S4. Different from the situation in Zhejiang Province, only

PFOA predominated total PFASs with a mean concentration of 88 ng/L (Table S4). After PFOA were PFHxA and PFBS, which were detected with lesser ranges of 4.0-16 ng/L and 4.6-12 ng/L, respectively. PFOS and other individual PFASs also occurred at lesser concentrations. Compared with other industrial areas around the world, Shanghai and Kunshan were more contaminated by PFOA than those for Vietnam (Kim et al., 2013), German, Spanish (Llorca et al., 2012), Tokyo (Zushi et al., 2011), France (Labadie and Chevreuil, 2011) and Tianjin (Pan et al., 2011) and Shenyang in China (Sun et al., 2011) (Table S5), but less than those for Wuhan (Wang et al., 2013) and Fuxin (Bao et al., 2011) in China (Table 1). This indicated PFOA was largely used in industrial production in China, and the fluorine chemical industry was likely the main source of PFASs (Xiao et al., 2012; Yan et al., 2012). A high value of 210 ng/L sum-PFASs found in SH1 may be attributed to discharges from most wastewater plants (WWTPs) in Shanghai, which have been determined to be the major sources of PFASs to surface water (Sun et al., 2011). Compared with a former study in Shanghai (So et al., 2007), at the location (named SH3 in former study) that is near location SH1 in this study, a decrease of PFOS and PFOA was observed (Table 1), confirming that restrictions for C8 compounds are functioning.

3.4 Mass loadings of PFASs to the East Sea

PFASs are expected to mainly remain in the water column and thus can be transported with riverine flows based on their solubilities and persistences (Boulanger et al., 2005). Our study area is a typical source of PFAS emission in east China. To evaluate the emissions of PFASs from the source area to the coastal waters of China even to the global waters, we calculated PFAS discharges according to Equation 1 (Sun et al., 2011).

$$\text{Mass flow} = C_{\text{water}} * F_{\text{water}} \qquad (1)$$

Where: C_{water} is PFAS concentration in water (ng/L) and F_{water} is the river flux. Corresponding half of the MDL values were used if the concentrations of the samples were less than the MDL. Bioaccumulation, sorption to particles or appreciable chemical transformation were neglected.

Fluxes and mass flows of individual PFASs in rivers are shown (Table 2). PFASs measured at mouths of rivers in each basin represent the overall aqueous loads in the corresponding river basin and the seasonal variation in the discharges was not considered, and concentrations of PFASs were dissolved fractions of samples. The Huangpu and Qiantang Rivers (SH1 and ZJ7) exhibited relatively large mass flows of sum-PFASs of 2100 and 1400 kg/year, respectively, to the East China Sea. The Huangpu River transported 1800 kg PFOA/year, followed by Qiantang River and Yong River (ZJ22) with 850 kg/year and 140 kg/year, respectively (Table 2). A discharge of 460 kg PFHxA/year came from the Qiantang River, followed by 110 kg/year from the Huangpu River, which indicates that the Qiantang River contributed more PFHxA to the East China Sea every year. All the rivers studied flow directly into the East China Sea, expect that the Huangpu River, which joins the Yangtze River before it finally runs into the East China Sea. Thus, more than 4000 kg PFASs (existed in aqueous phase) were discharged into the East China Sea and even spread to the ocean every year.

In comparison with other rivers in the world, the mass flow of sum-PFASs of Huangpu River (2100 kg/year) was greater than those in the Ebro River with a flow of 31 kg/year (Sánchez-Avila et al., 2010) and the Elbe River with a flow of 113 kg/year to North sea (Ahrens et al., 2009b), while were lower than the Po River with a flow of 2628 kg/year (Loos et al., 2008). Alternatively, mass flows of other individual PFASs in present study were less, especially for PFOS. The flux of Hanjiang River in Wuhan city was even as small as 69.8 m^3/s, but the great concentration of PFOS from the Hanjiang River resulted in a relatively great mass flow of 130 kg PFOS/year (Wang et al., 2013), which was greater than any river in present study. Mass flow evaluation is essential to determine the pollution of a river and to the ocean rather than the concentration or the flux singly.

3.5 Correlations of individual PFASs and influence factor analysis

Relationships among PFASs and identification of sources of PFASs in surface waters of eastern China were investigated by use of pairwise correlations and factor analyses. Two regions, Shanghai and Kunshan (n=10) and Zhejiang Province (n=29), were analyzed by use of Spearman rank correlation analysis (Table S6). In Zhejiang Province, except for FOSA, most of the PFASs were positively correlated, regardless of whether they were PFSAs or PFCAs, which indicates common sources for most of the PFASs. However, for Shanghai and Kunshan, no correlations were found between the PFASs (C4, C6-C8), but strong correlations were observed among longer-chain PFCAs (>C6). PFOA mainly came from industrial manufacture while PFHpA, PFNA, PFDA and PFUnDA were possibly from degradation of fluorotelomer alcohols (FTOHs) (So et al., 2007; Möller et al., 2010) because concentrations of those compounds were less in the study area. In the Shanghai-Kunshan region, PFHxA was positively correlated with PFOA (r^2=0.661, p=0.05) but negatively correlated with FOSA (r^2=-0.677, p=0.05). Therefore, it is likely that PFHxA and FOSA were released from different sources. PCA also shows the same result that longer-chain PFCAs (C>8) have positive correlation with the first principal component (PC1). PFSAs were observed similar principal component composition. And compared with PFHxA that positively correlated with PC2, FOSA has negative correlation in PC2, indicating different principal components between the two compounds (Figure 3). Results of previous studies have shown that FOSA was related to degradation of precursors like N-ethylperfluorooctane sulfonamide (N-EtFOSA) and perfluorooctane sulfonamide acetate (FOSAA) (Rhoads et al., 2008; Plumlee et al., 2009). PFHxA was probably related to the industry similar to PFOA, which was consistent with previous study indicating that high levels of PFHxA or PFOA precursors in WWTPs probably came from industrial sources (Xiao et al., 2012). The result was agreement with the conclusion that PFHxA was used as new material in manufacture industry of Zhejiang Province, China.

4. Conclusions

In the present study, concentrations of 17 PFASs were measured in surface waters at 39 sampling sites in eastern China. Comparing the results with those of previous studies, concentrations of PFOS were lower, but relatively great concentrations of PFHxA were observed. This confirms that global restrictions on PFOS are having an effect on concentrations in surface waters in China. The appearance of relatively great concentrations of PFHxA in Zhejiang Province is likely the result of using PFHxA or ammonium perfluorohexanoate, APFHx as replacements for PFOA or ammonium perfluorooctanoate, APFO in fluoropolymer polymerization. PFHxA, also PFBS are considered to be less hazardous because of their lesser acute toxicity and bioaccumulation compared to C8 compounds, such as PFOA and PFOS, but they are as persistent in the environment as the longer-chain homologues. Thus, the current increasing global production and use of these chemicals and their potential precursors will lead to increasing widespread environmental and human exposure to these chemicals, more attention should be paid to their ecological risk because of their increasing discharge volume and property of long-range transportation by its precursors. It is important to remain vigilant that there are uncertainties and knowledge gaps about the shorter chain homologues and that the long-term accumulations of these products in the environment need to be assessed.

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Appendix A. Supplementary data

Supplementary data to this article can be found online.

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Figure 1. Spatial distributions of concentrations of sum-PFASs in surface waters in eastern China.

Figure 2. Profile of relative contributions of individual PFASs to sum-PFASs in surface waters of eastern China

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Table 1: Comparison of typical individual PFASs in the surface waters in China.

Type	Sampling date	Site	PFOS	PFHxA	PFOA	PFNA	PFDA	∑PFAS	Area description	Reference
Lake	2011.5-2011.7	West Lake	0.35	53.2	84.6	0.5	0.2	145.93	Urban area	This study
	2011.5-2011.7	Taihu (n=2)	2.0-2.8	$9.4\text{-}1.0\times10^1$	$2.0\times10^1\text{-}2.3\times10^1$	1.0-1.2	0.42-0.57	$4.3\times10^1\text{-}4.5\times10^1$	Lake inlet	This study
	2011.7	Taihu	1.5×10^1	1.9×10^1	5.6×10^1	2.6	1.5	1.0×10^2	industrial area	Yu et al., 2013
			$8.5\text{-}2.1\times10^1$	$1.5\times10^1\text{-}3.1\times10^1$	$2.3\times10^1\text{-}7.1\times10^1$	1.9-3.8	1.1-2.4	$6.0\times10^1\text{-}1.3\times10^2$		
	2009.11-2009.12	Taihu	2.7×10^1	na**	2.2×10^1	nd**	nd	5.2×10^1	Whole lake	Yang et al., 2011
			$3.6\text{-}4.0\times10^2$	na**	$1.1\times10^1\text{-}3.7\times10^1$	nd**	nd	$1.8\times10^1\text{-}4.5\times10^2$		
	2009.2-2009.4	Taihu	3.5-9.4	nd	25-34	2.3-3.6	<2.5	-**	Lake shore water	Qiu et al., 2010
	2008.5	Guanting Reservoir	nd-0.52	nd	0.55-2.3	nd	nd-0.23	0.70-3.1	Dringking water source	Wang et al., 2011
	2011.5-2011.7	Tangpu Reservoir	<0.07	0.15	1.28	0.17	0.07	2.09	Town area	This study
		Changtan Reservoir	<0.07	0.12	0.47	0.11	0.05	0.99	Rural area	
		Hongqiao Reservoir	<0.07	0.21	2.85	0.24	0.1	3.68	Town area/Fishery	
		Cengang Reservoir	0.69	0.49	7.88	0.41	0.09	11.07	Town area/Fishery	
River	2004.11	shanghai	$1.2\times10^1\text{-}1.4\times10^1$	5.0-5.3	$2.3\times10^2\text{-}2.6\times10^2$	$9.0\text{-}1.0\times10^1$	3.3-3.8	-	Urban area/Industry area	So et al., 2007
	2008.12	Haihe River,	1.1-7.7	na	$4.7\text{-}2.3\times10^1$	0.29-2.2	0.12-1.0	-	Urban area/Industry	Pan et al., 2011

	Tianjin							area	
2009.8	Fuxin	0.28-0.54	na	2.7×10^{1}-6.7×10^{2}	0.43-1.6×10^{1}	<0.10-2.1×10^{1}	3.7×10^{2}-7.1×10^{2}	Urban area/Industry area	Bao et al., 2011
2009.9	Shenyang	0.66-1.6×10^{1}	1.3-3.7×10^{1}	9.2-2.5×10^{1}	nd-5.2	nd-1.2	1.7×10^{1}-2.4×10^{2}	Urban area/Industry area	Sun et al., 2011
2009.9	Hun River, Liaoning	0.4-3.3	1.3 -3.8×10^{1}	1.8-1.1×10^{1}	nd-1.6	nd-0.66	-	Urban area	Sun et al., 2011
2009.11-2009.12	Liao River	0.33	na	1.1×10^{1}	nd	nd	4.4×10^{1}	Urban and industrial area	Yang et al., 2011
		n.d.-6.6	na	n.d.-2.8×10^{1}	nd	nd	1.4-1.3×10^{2}		
2009	Victoria Harbour, Hongkong	0.030-1.2	0.15-0.97	0.31-1.9	0.032-0.40	0.014-0.31	-	Urban area	Loi et al., 2013
2010.4	Wuhan	5.2×10^{1}	nd	8.1×10^{1}	1.9×10^{1}	2.8×10^{1}	2.0×10^{2}	Urban area/Industry area	Wang et al., 2013
		nd-8.9×10^{1}	nd	2.5 -2.6×10^{2}	nd-.4×10^{1}	nd-9.5×10^{1}	8.6-5.7×10^{2}		
2011.3	Huaihe	4.7	0.62	1.8×10^{1}	0.91	0.33	2.8×10^{1}	Industrial area	Yu et al., 2013
		1.4-2.5×10^{1}	<0.10-1.5	6.2-4.7×10^{1}	0.67-1.4	<0.10-1.0	1.1×10^{1}-7.9×10^{1}		
2011.5-2011.7	Hangzhou Bay	1.04	24.99	44.63	0.69	0.31	77.25	Coastal area	This study
	Qiantang River	0.41	31.11	57.27	0.66	0.31	97.45	Urban area	
	Cao’e River	0.24	0.76	4.82	0.54	0.37	9.00	Middle stream	
	Fenghua River	2.82	2.67	52.89	1.07	0.48	66.18	Town area	
	Yong River	1.60	2.39	39.21	1.01	0.35	52.91	Town area	

	Yuyao River	3.38	3.17	37.31	1.5	0.73	64.33	Town area	
	Ou River	<0.07	0.15	0.64	0.12	0.05	1.25	Rural area	
	Feiyun River	0.24	0.43	1.7	0.09	<0.02	3.25	Rural area	
	Jiao River	5.04	1.02	4.34	0.8	0.33	15.22	Rural area	
2011.5-2011.7	Shanghai	2.98	10.56	182.25	2.21	1.34	212.41	Urban area/Industry area	This study

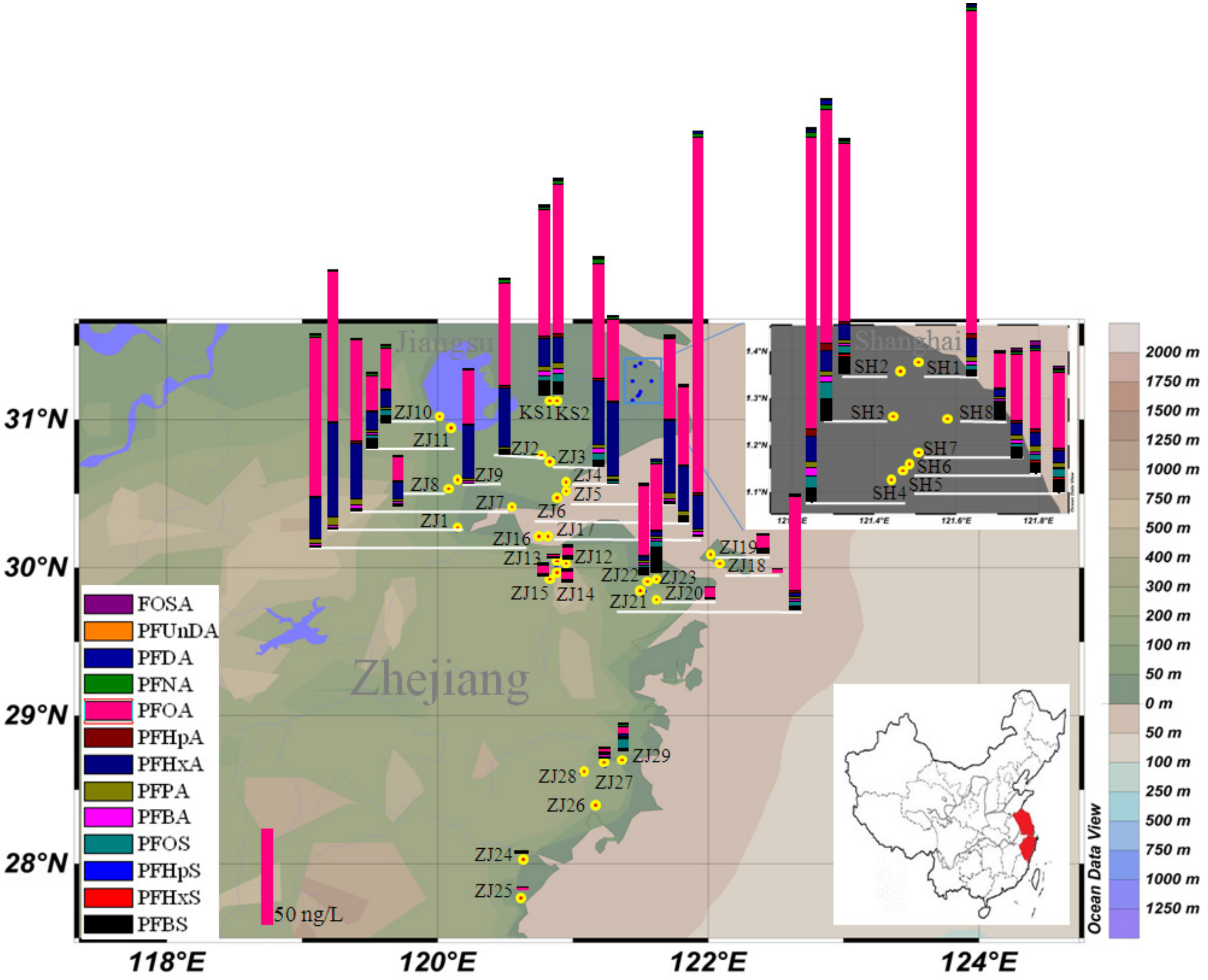
* ZJ16 and ZJ17 directly collected from sewage outlets (inner and out sluice gate) were not taken into the calculation of mean concentration and the range of Cao’e River

** na = not analysed; nd = not detected; “-“ not given in the literature

Table 2: Flux estimation of dissolved fractions of PFASs in selected rivers of eastern China (kg /year).

Name	Discharge (m^3/s)	PFOS	PFOA	PFNA	PFHxA	∑PFAS
Huangpu River	320.3	3.0×10^{1}	1.8×10^{3}	2.2×10^{1}	1.1×10^{2}	2.1×10^{3}
Qiantang River	470.3	6.1	8.5×10^{2}	9.8	4.6×10^{2}	1.4×10^{3}
Cao’e River	143.6	1.0	2.2×10^{1}	2.3	3.4	4.1×10^{1}
Yong River	111.0	5.6	1.4×10^{2}	3.5	8.4	1.9×10^{2}
Fenghua River	53.5	4.7	8.9×10^{1}	1.9	4.6	1.1×10^{2}
Yuyao River	52.1	5.6	6.1×10^{1}	2.5	5.3	1.1×10^{2}
Jiao River	163.9	2.6×10^{1}	2.2×10^{1}	4.1	5.3	7.8×10^{1}
Ou River	619.9	0.78	1.3×10^{1}	2.2	3.0	2.5×10^{1}
Feiyun River	126.8	0.96	6.8	0.3	1.7	1.3×10^{1}

Figure 1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121.4°E
121.6°E
121.8°E
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SH5
SH6
SH7
SH8
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KS2
ZJ1
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1250 m
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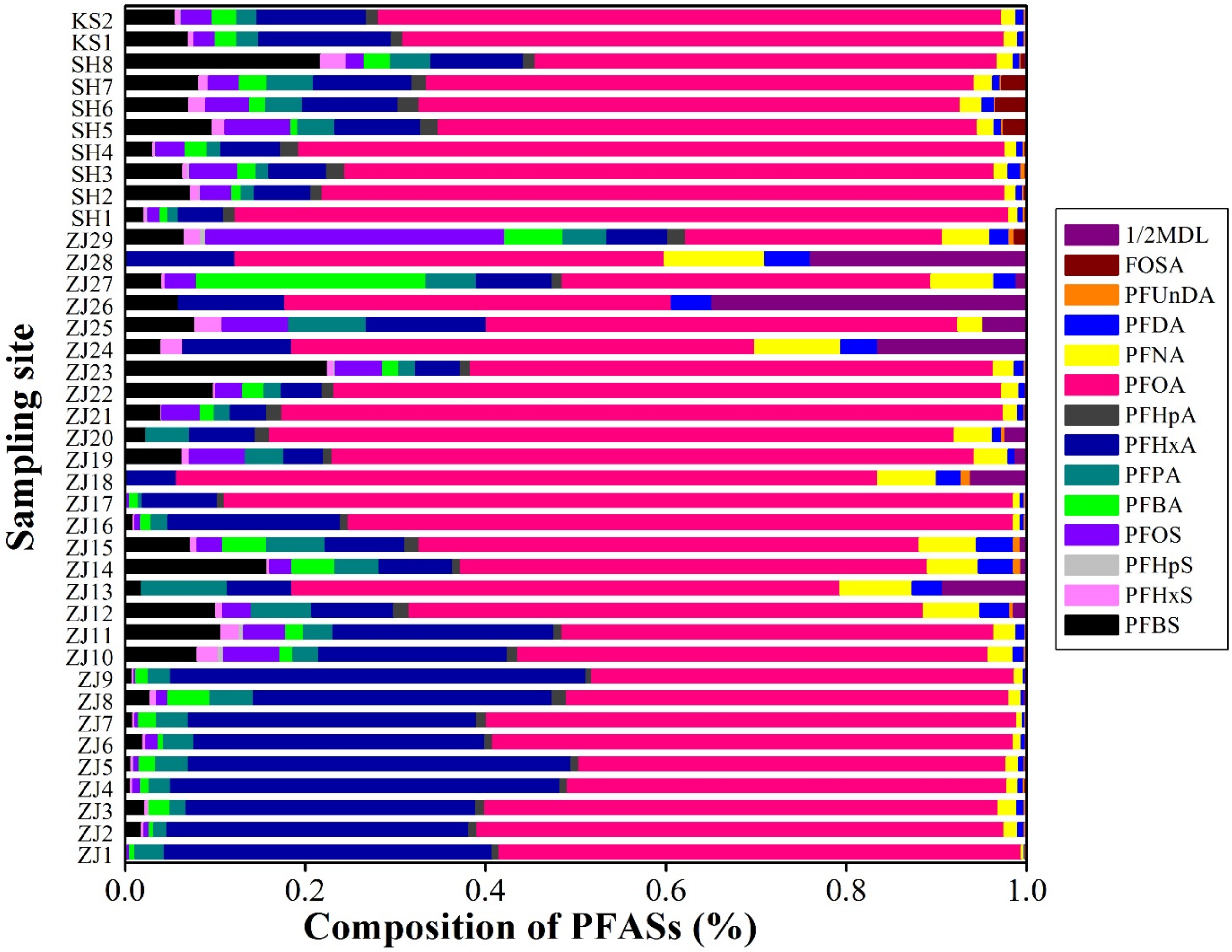
Ocean Data View

Figure 2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Composition of PFASs (%)
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PFUnDA
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PFNA
PFOA
PFHpA
PFHxA
PFPA
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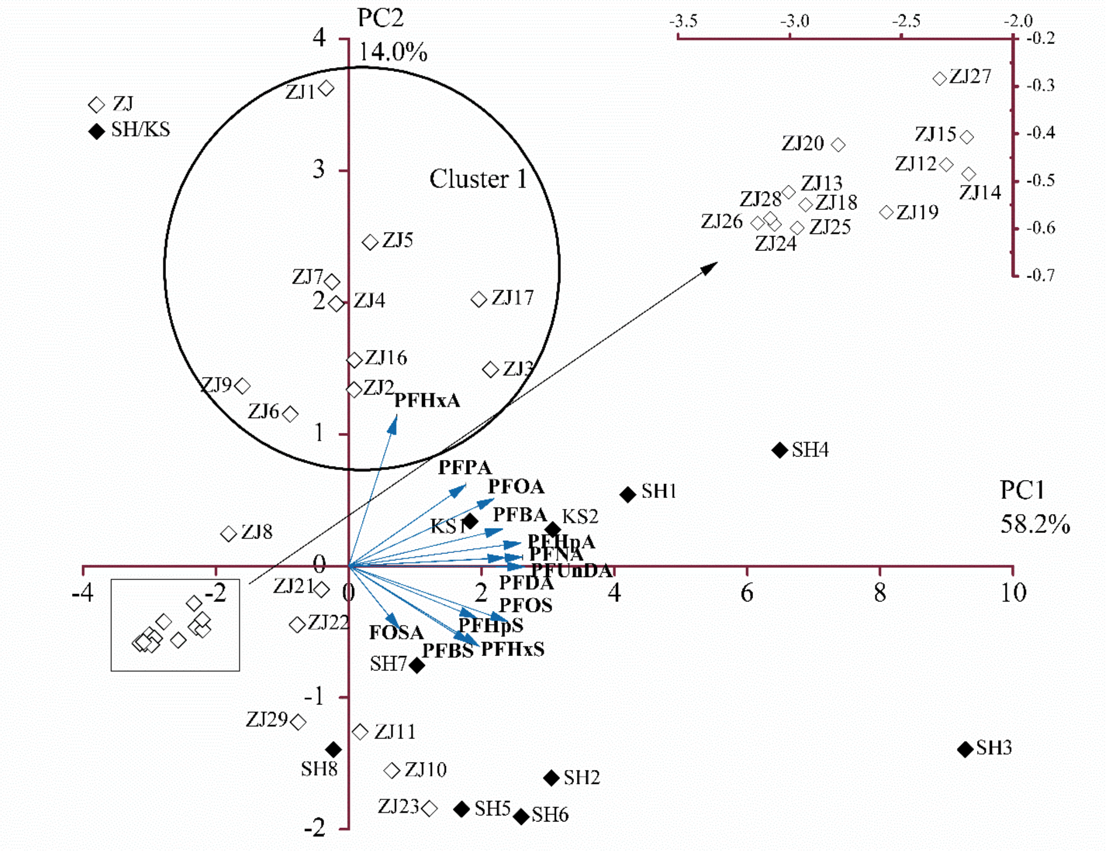
PFOS
PFHpS
PFHxS
PFBS

Figure 3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