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# Distribution characteristics of poly- and perfluoroalkyl substances in the Yangtze River Delta

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## ABSTRACT

In this work, a method was developed and optimized for the analysis of polyfluoroalkyl and/or perfluoroalkyl substances (PFASs) content in surface water and sediment samples with high instrumental response and good separation. Surface water and sediment samples were collected from the Yangtze River Delta (YRD) to analyze the distribution characteristics of perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSA), perfluoroalkyl phosphonic acids (PFPA), perfluoroalkyl phosphinic acids (PFPIAs), and polyfluoroalkyl phosphoric acid diesters (diPAPs). The results showed that the total concentrations of PFCAs and PFSA in YRD varied from 31 to 902 ng/L. PFCAs ( $\geq 11$  carbons) and PFSA ( $\geq 10$  carbons atoms) were not detected in any surface water samples. The mean concentrations of all PFCAs and PFSA in surface water from the sampling areas decreased in the following order: Yangtze river (191 ng/L)  $\approx$  Taihu lake (189 ng/L)  $>$  Huangpu river (122 ng/L)  $\approx$  Qiantang river (120 ng/L)  $>$  Jiaying urban river (100 ng/L). Strong significant ( $p < 0.05$ ) correlations between the concentrations of many of the compounds were found in the sampling areas, suggesting a common source for these compounds. Only perfluorooctanoic acid (PFOA) was observed in all sediment samples, at concentrations varying from 0.02 to 1.35 ng/g. Finally, detection rates of two diPAPs were only 8% and 10%, respectively and the concentration of diPAPs was two to three times lower compared to PFCAs and PFSA.

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## Introduction

Polyfluoroalkyl and/or perfluoroalkyl substances (PFASs) are anthropogenic chemicals with a fluoroalkyl backbone (F (CF<sub>2</sub>)<sub>x</sub>) and a polar head group (i.e., sulfonic acid, carboxylic acid, or phosphonic acid). This particular molecular structure imparts oleophobic and hydrophobic properties to these chemicals (Kissa, 2001). PFASs have extensive applications in industrial and commercial products, including in non-stick, grease-proofing and surface treatment applications due to their high

surface activity and ability to repel water, oil, and stains. Their extensive applications and ability to resist biological and environmental degradation have led to the ubiquitous presence of perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSA) in environmental samples, including surface water (De Silva et al., 2011; D'eon et al., 2009a; Hansen et al., 2002; Mak et al., 2009), groundwater (Moody et al., 2003; Murakami et al., 2009; Schultz et al., 2004), sea water (So et al., 2004; Yamashita et al., 2005), sediments (Bečanová et al., 2016; Pan et al., 2014), soil (Li et al., 2010), air (Sinclair et al., 2007), and

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dust (Haug et al., 2011; Kubwabo et al., 2005; Shoeib et al., 2005), as well as in human sera (Hansen et al., 2001; Hölzer et al., 2008; Houde et al., 2006a; Vestergren and Cousins, 2009) and animal sera and livers (Ahrens et al., 2009; Houde et al., 2006b; Lau et al., 2007; Martin et al., 2003). Previous studies have assessed the distribution, transport, fate and sources of PFCAs and PFSAs, demonstrating the biotransformation of precursors into PFCAs and perfluorooctane sulfonate anion (PFOS) in microbial and soil systems (Russell et al., 2008; Wang et al., 2011), as well as in vitro (Martin et al., 2005; Nabb et al., 2007; Tomy et al., 2004; Benskin et al., 2009) and in vivo animal models (D'eon and Mabury, 2007, 2010; Fasano et al., 2009).

Recently, more types of PFASs have been detected in environmental samples, including perfluoroalkyl phosphonic acids (PFPA), perfluoroalkyl phosphinic acids (PFPIAs), polyfluoroalkyl phosphoric acid monoesters (monoPAPs), and polyfluoroalkyl phosphoric acid diesters (diPAPs), among others. It was reported that PFPA and PFPIAs were in the list of high production volume perfluoroalkyl acids (4500–227,000 kg/year) in 1998 and 2002 (Howard and Meylan, 2009). These compounds were commonly used as defoaming agents in pesticide formulations in USA (Heid et al., 1975) until their application was banned in 2008 (US EPA, 2006). The first report of PFPA and PFPIA detection in environmental samples was from Canada, where PFPA was observed in 80% of surface water samples at concentrations in the picogram to low nanogram per liter range and in six of the seven waste water treatment plants (WWTPs) effluent samples assessed (D'eon et al., 2009a). Perfluorooctyl phosphonic acid (C8-PFPA) was also detected at a concentration of 1 ng/L in Dutch surface water samples (Esparza et al., 2011). In lake trout collected from Lake Ontario, PFPIAs were identified at concentrations of one to two orders of magnitude lower than those of PFCAs and PFSAs (Guo et al., 2012). Human exposure to PFPIAs was confirmed in USA, where 6:6 PFPIA and 6:8 PFPIA were found in human sera at a concentration range of 4–38 ng/L (Lee and Mabury, 2011). In another study, PFPA (C6, C8) and PFPIAs (C6/C6, C6/C8, and C8/C8) were also detected in human sera in Germany and China (Yeung and Mabury, 2016).

Another class of PFASs, polyfluoroalkyl phosphoric acid esters (PAPs), are not only used as grease-proofing agents in food contact paper, but may also be found in cosmetics, hair and personal care products, floor waxes, paints and finishes, and cleaning fluids (US FDA, 2003). DiPAPs have been detected in Canadian WWTP sludge and paper fiber extracts at concentrations ranging from  $47 \pm 22$  to  $200 \pm 130$  ng/g and  $34 \pm 30$  to  $2200 \pm 400$  ng/g, respectively (D'eon et al., 2009b). Further, high concentrations of diPAPs (up to 7000 ng/g) were reported in dust samples collected from Canada, Faroe Islands, Sweden, Greece, Spain, Nepal, Japan, and Australia (De Silva et al., 2012; Eriksson and Karrman, 2015). Direct evidence of human exposure to diPAPs was obtained by the detection of diPAPs in human sera collected in USA in sub part-per-billion (ppb) to ppb levels (D'eon et al., 2009b; Lee and Mabury, 2011). Additionally, studies have demonstrated the degradation of diPAPs to PFCAs in WWTPs (Lee et al., 2010) and their biotransformation in rats (D'eon and Mabury, 2007). Therefore, diPAPs are important both as a precursor to PFCAs and potentially as a fluorinated contaminant on their own. As PAPs are primarily used in food contact paper products, mono-

di- and tri-substituted PAPs have been found in food packaging materials in the Swedish market, with up to nine congeners of diPAPs being detected in food samples (0.9 to 36 pg/g) (Gebink et al., 2013). These results indicate that consumption of food packed in PAP-containing materials is an indirect source of human exposure to PFCAs. Nevertheless, compared to PFCAs and PFSAs, little is known about the environmental occurrence and fate of PFPA and diPAPs, particularly in China.

The Yangtze River Delta (YRD) region, with a population of 150 million people, has experienced rapid economic growth in the past three decades. It is one of the most economically dynamic and wealthy regions in China, with the highest degree of openness and innovation. The region includes several metropolises like Shanghai and the capital cities of Hangzhou, Suzhou, and Nanjing as well as medium-sized cities like Ningbo and Wuxi, among others. The chemical engineering, textile, and paper making industries are important components of the YRD industry, all of which are potential sources of PFASs. The Yangtze, Huangpu, and Qiantang rivers as well as the Taihu lake and Jiaying urban river, all of which are located in the YRD, are important drinking water sources for the region.

The consumption of PFAS contaminated drinking water or fish may pose a health risk to aquatic organisms, wildlife, and humans. Thus, the objectives of this study were to investigate the contamination profiles of 23 PFASs (11 PFCAs, 4 PFSAs, 3 PFPA, 3 PFPIAs and 2 diPAPs) in water and sediment samples collected from the middle and lower reaches of the Yangtze, Huangpu, and Qiantang rivers, Jiaying urban river and Gonghu region of Taihu lake; as well as to explore the factors influencing PFAS distribution between water and sediment.

## 1. Materials and methods

### 1.1. Chemicals and reagents

The target analytes included PFCAs (C4–C14), PFSAs (C4, C6, C8, and C10), PFPA (C6, C8, and C10), PFPIAs (C6/C6, C8/C8, and C6/C8), and diPAPs (6:2 and 8:2). The category, name and acronym of all the analytes are shown in Table 1. Mass-labeled PFASs standards include perfluoro-*n*- $^{13}\text{C}_4$ ]butanoic acid ( $^{13}\text{C}_4$ -PFBA), perfluoro-*n*- $^{13}\text{C}_2$ ]hexanoic acid ( $^{13}\text{C}_2$ -PFHxA), perfluoro-*n*- $^{13}\text{C}_4$ ]octanoic acid ( $^{13}\text{C}_4$ -PFOA), perfluoro-*n*- $^{13}\text{C}_5$ ]nonanoic acid ( $^{13}\text{C}_5$ -PFNA), perfluoro-*n*- $^{13}\text{C}_2$ ]decanoic acid ( $^{13}\text{C}_2$ -PFDA), perfluoro-*n*- $^{13}\text{C}_2$ ]undecanoic acid ( $^{13}\text{C}_2$ -PFUnDA), perfluoro-*n*- $^{13}\text{C}_2$ ]dodecanoic acid ( $^{13}\text{C}_2$ -PFDoA), sodium perfluorohexane- $^{18}\text{O}_2$ ]sulfonate ( $^{18}\text{O}_2$ -PFHxS), sodium perfluoro [ $^{18}\text{O}_2$ ]octanesulfonate ( $^{18}\text{O}_2$ -PFOS), sodium bis(1H,1H,2H,2H- $^{13}\text{C}_2$ ]perfluorooctyl)phosphate ( $^{13}\text{C}_4$ -6:2 diPAP) and sodium bis(1H,1H,2H,2H- $^{13}\text{C}_2$ ]perfluorodecyl)phosphate ( $^{13}\text{C}_4$ -8:2 diPAP). All native and mass labeled standards were purchased from Wellington Laboratories (Guelph, Canada). Liquid chromatogram-mass spectrum (LC-MS) grade methanol, acetonitrile, methyl-*tert*-butyl ether (MTBE), and ammonium acetate were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Analytical grade sodium hydroxide (NaOH) was purchased from Sinopharm Chemical Reagent, Beijing, Co., Ltd., China. Tetra-butyl ammonium hydrogen sulfate (TBAS) was purchased from J.T. Baker (Phillipsburg, NJ, USA). Ottawa sand was purchased from

**Table 1 – Category, name and acronyms of target analytes.**

Category	Name	Acronyms
Perfluoroalkyl carboxylic acids (PFCAs) $C_nF_{2n-1}O_2$	Perfluorobutanoic acid	$n = 4$ , PFBA
	Perfluoropentanoic acid	$n = 5$ , PFPeA
	Perfluorohexanoic acid	$n = 6$ , PFHxA
	Perfluoroheptanoic acid	$n = 7$ , PFHpA
	Perfluorooctanoic acid	$n = 8$ , PFOA
	Perfluorononanoic acid	$n = 9$ , PFNA
	Perfluorodecanoic acid	$n = 10$ , PFDA
	Perfluoroundecanoic acid	$n = 11$ , PFUnDA
	Perfluorododecanoic acid	$n = 12$ , PFDoDA
	Perfluorotridecanoic acid	$n = 13$ , PFTTrDA
	Perfluorotetradecanoic acid	$n = 14$ , PFTeDA
Perfluoroalkylsulfonates (PFASs) $C_nF_{2n+1}SO_3^-$	Potassium perfluorobutanesulfonate	$n = 4$ , PFBS
	Sodium perfluorohexanesulfonate	$n = 6$ , PFHxS
	Sodium perfluorooctanesulfonate	$n = 8$ , PFOS
	Sodium perfluorodecanesulfonate	$n = 10$ , PFDS
Perfluoroalkyl phosphonic acids (PFPAs) $C_nF_{2n+1}PO_3^{2-}$	Perfluorohexyl phosphonic acid	$n = 6$ , C6-PFPA
	Perfluorooctyl phosphonic acid	$n = 8$ , C8-PFPA
	Perfluorodecyl phosphonic acid	$n = 10$ , C10-PFPA
	Bis(perfluorohexyl)phosphinate	$n = 6, m = n$ , C6/C6-PFPIA
Perfluoroalkyl phosphinic acids (PFPIAs) $C_nF_{2n+1}C_mF_{2m+1}PO_2^-$	Bis(perfluorooctyl)phosphinate	$n = 8, m = n$ , C8/C8-PFPIA
	Perfluoro(hexyloctyl)phosphinate	$n = 6, m = 8$ , C6/C8-PFPIA
Polyfluoroalkyl phosphoric acid diesters (DiPAPs) $(C_n + 2F_{2n+1})_2PO_4H_9$	6:2 Fluorotelomer phosphate diester	$n = 6$ , 6:2 diPAP
	8:2 Fluorotelomer phosphate diester	$n = 8$ , 8:2 diPAP

Fisher Scientific (Pittsburgh, PA, USA). Oasis® weak anion exchange (WAX; 6 cm<sup>3</sup>, 150 mg) solid phase extraction (SPE) cartridges were purchased from Waters (Milford, MA, USA). Milli-Q water (purified using Milli-Q system, Millipore, USA, 18 M $\Omega$ ) was used throughout the experiment.

### 1.2. Sample collection

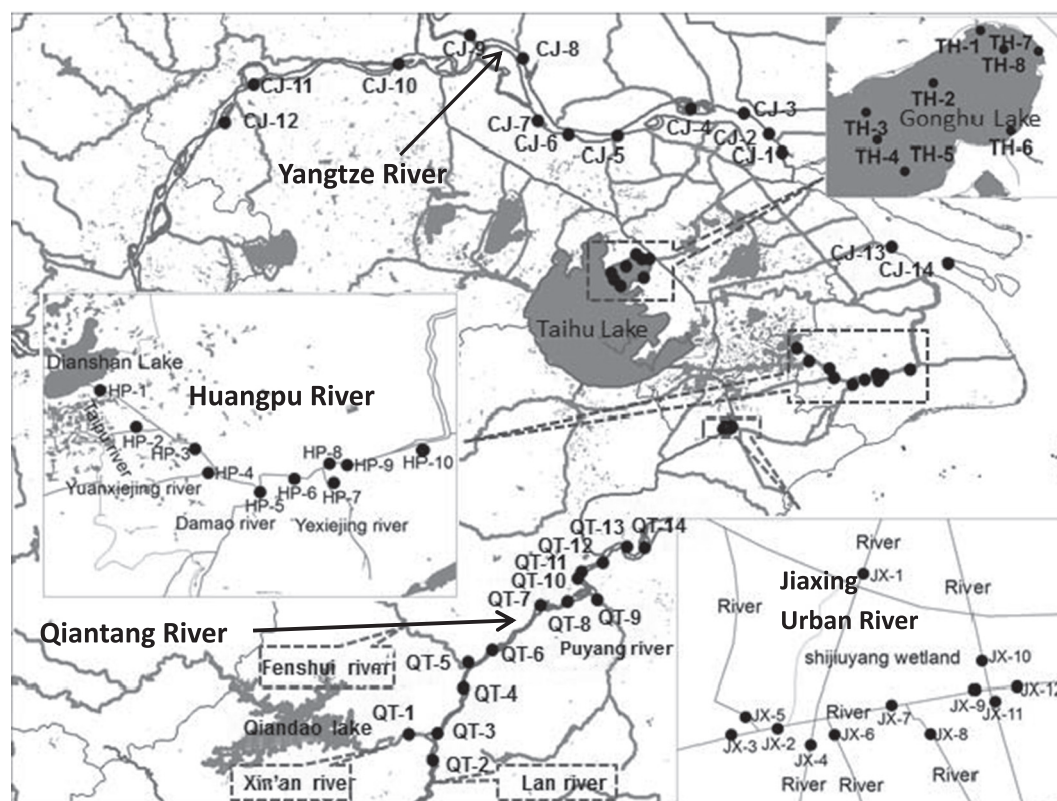
The YRD is an important area of economic growth in China, supporting extensive industrial activities, business, trade, transportation, agriculture, and aquaculture, and contributing 20% of the Chinese gross domestic production in 2014 (China NBS, 2014). However, with this rapid economic development, the regional environment is deteriorating (Shao et al., 2006; Zhang et al., 2013). The YRD is well known as “a land of rice and fish” reflecting the importance of water to the region. Surface water and sediment samples were collected in the middle and lower reaches of the Yangtze river (or Changjiang river; CJ), Qiantang river (QT), Huangpu river (HP), Jiaying urban river (JX) and Gonghu region of Taihu lake (TH) in April 2015 (abbreviations were used to label the samples retrieved from these water bodies and are used as such herein). All of the sampled rivers and lakes are current or previous drinking water sources for those living within the YRD region. Specifically, the Yangtze river serves the cities of Shanghai, Nanjing and Suzhou, among others; the Qiantang river serves Hangzhou city; the Huangpu river serves Shanghai city; Jiaying urban river serves Jiaying city; and Gonghu region of Taihu lake serves the cities of Wuxi and Suzhou. The sampling sites are shown in Fig. 1. One liter of surface water samples was collected in polypropylene (PP) bottles pre-rinsed with Milli-Q water and methanol. The sediment samples were retrieved with a portable bottom sampler and stored in stainless steel boxes. Immediately following collection, samples were kept at 4°C and shipped to the lab.

### 1.3. Sample preparation

Water samples were first filtered through a 0.45  $\mu$ m mixed cellulose membrane and then extracted with Oasis WAX cartridges (0.5 g, 6 cm<sup>3</sup>) (Waters, Corp., Milford, MA) following the published methods with minor modification (Taniyasu et al., 2005, 2008). Before SPE, 2 ng of mass-labeled PFSA was spiked into the water sample as an internal standard. The cartridges were preconditioned by passage of 6 mL of 1% NH<sub>4</sub>OH in methanol, followed by 6 mL of methanol and 6 mL of Milli-Q water. Water samples (1000 mL) were passed through the pre-conditioned cartridges at a rate of 5 mL/min. The cartridges were then washed (6 mL of 25 mmol/L ammonium acetate buffer at pH 4) and the target analyte was eluted twice with 6 mL of 1% NH<sub>4</sub>OH in methanol/acetonitrile at a 1:1 ratio. The eluates were then concentrated to 1 mL under a gentle stream of nitrogen.

Sediment samples were freeze-dried and homogenized with a mortar and pestle. The samples were extracted using the ion-pairing method, the details of which are described elsewhere (Guo et al., 2016). Before extraction, 2 ng of the internal standard was spiked into 1 g of sediment sample and shaken for 8 min. Then, 2.5 mL of 60/40 acetonitrile/0.2 mol/L NaOH solution was added to the pre-spiked sediment samples. The resulting solution was placed in an ultrasonic bath for 15 min and then centrifuged at 5000 r/min for 10 min. The supernatant was transferred to a 15 mL PP tube. The procedure was repeated once, and the supernatant was combined with the original extract. The extracts were reduced to approximately 1 mL using nitrogen evaporation. The resulting solution was mixed with 1 mL of 0.5 mol/L TBAS solution and the pH value of the mixed solution was adjusted to approximately pH 4 with 8 mol/L NaOH or 0.5 mol/L TBAS by dropwise addition. After mixing, 5 mL MTBE was added into the mixture and the solution was shaken for 10 min. The





**Fig. 1 – Sampling sites of Yangtze River (Water:  $n = 14$ , CJ-1–CJ-14; sediment:  $n = 12$ , CJ-1–CJ-10, CJ-12, CJ-14), Qiantang River (Water:  $n = 14$ ; QT-1–QT-14; sediment:  $n = 13$ , QT-1–QT-11, QT-13, QT-14), Huangpu River (Water:  $n = 10$ , HP-1–HP-10; sediment:  $n = 3$ , HP-2, HP-4, HP-5), Taihu Lake (Water:  $n = 7$ , TH-1, TH-2, TH-4–TH-8; sediment:  $n = 7$ , TH-1–TH-4, TH-6–TH-8) and Jiaying urban river (Water:  $n = 12$ ; JX-1–JX-12; sediment:  $n = 12$ , JX-1–JX-12).**

solution was centrifuged at 5000 r/min for 10 min and the top layer was transferred to another PP tube. The remaining aqueous solution was extracted with 5 mL MTBE once again, and after centrifugation, the removed top layers were combined. The MTBE aliquots were evaporated to dryness under a gentle stream of nitrogen, and reconstituted with 1 mL of methanol. Prior to instrumental analysis, the extract was divided into two vials with different solvent compositions to enhance sensitivity for the target compounds. For the analyses of PFCAs, PFSA, diPAPs and PFPIAs, equal parts of HPLC-grade water were added to the extract. For the analysis of PFPA, equal parts of 25 mmol/L of TBAS (pH 4) were added to the extract. Both vials were filtered with 0.2  $\mu\text{m}$  syringeless polypropylene filter.

#### 1.4. Instrumental analysis

The separation and analysis of PFASs was performed using ultra-pressure liquid chromatography with tandem mass spectrometry (UPLC–MS/MS). Waters Acquity UPLC was interfaced with a Xevo-TQD mass spectrometer (Xevo-TQD, Waters Corp, USA), operated in the electrospray negative ionization mode. The separation was carried out with Waters Acquity BEH C18 column (50 mm  $\times$  2.1 mm i.d., 1.7  $\mu\text{m}$ ). Two LC methods were applied to analyze the target compounds; gradient elution was used to separate different groups of compounds. For the analyses of PFCAs and PFSA, the mobile phase consisted of 10 mmol/L ammonium acetate in HPLC-

grade water (A) and 10 mmol/L ammonium acetate in 8:2 (v/v) methanol: acetonitrile (B). To analyze PFPIAs, diPAPs, and PFPA, the mobile phase was 0.1%  $\text{NH}_4\text{OH}$  in HPLC-grade water (A) and methanol (B). The flow rate was 300  $\mu\text{L}/\text{min}$  and a 10  $\mu\text{L}$  aliquot of extract was injected into the column. The multiple reaction monitoring (MRM) of target compounds and optimized mass spectrum parameters are presented in Table 2.

#### 1.5. Quality control

An internal calibration using mass-labeled internal standards was performed to quantify PFCAs, PFSA, and diPAPs; whereas PFPIAs were quantified using an external standard calibration curve. As no internal standard was available and matrix effects were observed for PFPA in sediment, a matrix-matched standard was used to quantify PFPA. No matrix effects were observed in the determination of PFCAs, PFSA, diPAPs, and PFPIAs in water and sediment samples. Seven-point (20, 50, 100, 200, 500, 1000, and 2000 ng/L) calibration curves for PFCAs, PFSA, PFPIAs and diPAPs were prepared with methanol:  $\text{H}_2\text{O}$  at a 1:1 ratio. For PFPA, 10 times higher concentration (200, 500, 1000, 2000, 5000, and 20,000 ng/L) calibration curves were prepared with methanol: TBAS (pH = 4) at a ratio of 1:1. The correlation coefficient ( $R^2$ ) of each target compound calibration was over 0.99. Recovery tests were performed in triplicate by spiking 1.0 ng of PFCAs and PFSA, 5.0 ng of PFPA, 2.5 ng of PFPIAs, and 2.0 ng of 6:2 diPAP and 8:2 diPAP into HPLC-grade

**Table 2 – Overview of tandem mass spectrometry (MS/MS) settings, recovery and method detection limit (MDL) of target compounds.**

Analyte	MRM <sup>a</sup>	Cone voltage (V)	Collision energy CE (V)	Internal standard	MRM	Recovery (mean ± sd)		MDL	
						Water	Sediment	Water (ng/L)	Sediment (ng/g)
PFBA	212.9 > 168.9 <sup>a</sup>	20	8	<sup>13</sup> C <sub>4</sub> -PFBA	217.0 > 172.0	98% ± 8%	68% ± 10%	0.2	0.05
PFPeA	262.9 > 218.9 <sup>a</sup>	20	8			96% ± 5%	73% ± 7%	0.2	0.05
PFHxA	313.0 > 269.0 <sup>a</sup> /168.9	16	10	<sup>13</sup> C <sub>2</sub> -PFHxA	315.0 > 270.0	110% ± 7%	75% ± 10%	0.1	0.2
PFHpA	362.9 > 319.0 <sup>a</sup> /168.9	18	16			105% ± 6%	90% ± 12%	0.1	0.2
PFOA	412.9 > 368.9 <sup>a</sup> /168.9	20	10	<sup>13</sup> C <sub>4</sub> -PFOA	416.9 > 371.9	97% ± 5%	89% ± 8%	0.1	0.02
PFNA	462.9 > 419.0 <sup>a</sup> /168.9	16	10	<sup>13</sup> C <sub>5</sub> -PFNA	468.0 > 423.0	103% ± 9%	75% ± 6%	0.2	0.05
PFDA	512.9 > 468.9 <sup>a</sup> /219.0	22	10	<sup>13</sup> C <sub>2</sub> -PFDA	515.0 > 470.0	76% ± 4%	75% ± 7%	0.1	0.05
PFUnA	563.0 > 519.0 <sup>a</sup> /319.0	20	18	<sup>13</sup> C <sub>2</sub> -PFUnDA	565.0 > 520.0	80% ± 7%	77% ± 3%	0.1	0.05
PFDoA	612.9 > 569.0 <sup>a</sup> /319.0	24	12	<sup>13</sup> C <sub>2</sub> -PFDoA	615.0 > 570.0	49% ± 6%	70% ± 5%	0.1	0.05
PFTra	663.0 > 619.0 <sup>a</sup> /319.0	20	18			50% ± 5%	65% ± 4%	0.2	0.2
PFTeA	713.0 > 669.0 <sup>a</sup> /319.0	20	18			50% ± 5%	79% ± 11%	0.2	0.2
PFBS	298.8 > 79.9 <sup>a</sup> /99.0	56	36	<sup>18</sup> O <sub>2</sub> -PFHxS	403.00 > 103.0	98% ± 8%	76% ± 9%	0.2	0.5
PFHxS	398.9 > 79.9 <sup>a</sup> /99.0	45	31			122% ± 12%	79% ± 7%	0.4	0.2
PFOS	498.9 > 79.9 <sup>a</sup> /99.0	60	39	<sup>18</sup> O <sub>2</sub> -PFOS	502.97 > 99.0	106% ± 4%	72% ± 6%	0.1	0.2
PFDS	599.0 > 80.0 <sup>a</sup> /99.0	80	45			113% ± 11%	70% ± 3%	0.4	0.2
C6-PFPA	399.0 > 78.9 <sup>a</sup>	48	28	No IS		67% ± 7%	73% ± 13%	0.3	0.4
C8-PFPA	499.0 > 78.9 <sup>a</sup>	54	36	No IS		86% ± 6%	80% ± 9%	0.6	0.6
C10-PFPA	599.0 > 78.9 <sup>a</sup>	64	44	No IS		106% ± 9%	70% ± 7%	0.3	0.4
6:6 PFPiA	701.0 > 401.0 <sup>a</sup> /101.0	96	50	No IS		86% ± 5%	90% ± 6%	0.08	0.1
6:8 PFPiA	801.0 > 501.0 <sup>a</sup> /401.0 <sup>a</sup>	108	58	No IS		82% ± 4%	92% ± 8%	0.05	0.05
8:8 PFPiA	901.0 > 501.0 <sup>a</sup> /63.0	100	62	No IS		70% ± 3%	95% ± 9%	0.1	0.1
6:2 diPAP	789.0 > 443.0 <sup>a</sup> /97.0	52	20	<sup>13</sup> C <sub>4</sub> -6:2 diPAP	793.0 > 445.0	101% ± 6%	88% ± 11%	0.05	0.06
8:2 diPAP	993.0 > 545.0 <sup>a</sup> /97.0	48	24	<sup>13</sup> C <sub>4</sub> -8:2 diPAP	989.0 > 543.0	95% ± 8%	84% ± 8%	0.2	0.2

MRM: multiple reaction monitoring; IS: internal standard.

<sup>a</sup> Quantification ion.

water and Ottawa sand. The recovery results are given in Table 3. A quality control standard sample (Part No. 186004597, Waters, USA; containing 8 PFCAs (C5–C12) and 5 PFSAAs (C4, C6, C7, C7 and C10) in methanol) was analyzed to validate the developed method and the results were consistent with the quality control sample. The limit of detection and limit of quantification were defined as the concentrations producing a signal to noise ratio of 3 and 10, respectively. The method's detection limits (MDLs) were determined as three times the standard deviation of 10 parallel blank samples spiked with the lowest concentration of target compounds that could produce a signal to noise ratio of 10 (Table 2). No detectable target compounds were found in HPLC-grade water and Ottawa sand. Matrix interference, in the form of suppressed instrument response, was observed while analyzing PFPAs in sediment samples; therefore, matrix-matched standard calibration curves were applied to quantify PFPAs in sediment samples. The matrix-matched standards were prepared as described in Section 1.3 without spiking mass-labeled standards. After obtaining the final 1 mL extract, the extract was separated into seven fractions. To each fraction, we added the same volume of PFPFA standards at varying concentrations to prepare seven point (200, 500, 1000, 2000, 5000, and 20,000 ng/L) calibration curves. No target compounds were detected in procedural blanks (HPLC-grade water and sand). To check the stability of the instrument, one quality control standard was injected after every 10 sample injections. If the measured concentrations of quality control standards were not within ±20% of their corresponding theoretical values, then a new calibration curve was prepared. Values below limit of quantification were reported as not detected (ND) and a value of

“zero” was assigned for the calculation. Two procedural blanks were used with each set of 15–20 samples.

### 1.6. Total organic carbon content

The total organic carbon content (TOC) in water and sediment was analyzed with an Analytikjena multi N/C 2100S system (N/C 2100S, Jena, Germany). The water samples were filtered with 0.45 µm mixed cellulose ester membrane (Whatman GmbH, Germany) and acidified to pH 2 with HCl. For sediment samples, prior to instrumental analysis, the inorganic carbon was removed by steeping 50 mg of sediment into 0.1 mol/L HCl and heating the mixture to boiling for 3 min. The mixture was then heated in an oven at 105–110°C for 8 hr.

### 1.7. Statistical analyses

In order to evaluate the distribution patterns of PFASs and the relationships among the samples, factor analysis and hierarchical cluster analysis were performed with Statistical Product and Service Solutions (SPSS) 13.0 software (SPSS Inc., USA). The significance level was set at  $p < 0.05$ .

## 2. Results and discussion

### 2.1. Method optimization

The compositions of the mobile phase and the sample solvent were optimized to obtain better sensitivity and a symmetric

Table 3 – Comparison of PFOA and PFOS in freshwater samples from previous study.

Sampling water body	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFBS	PFHxS	PFOS	PFDS	Reference
	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	
Qiantang River in Huangzhou section	ND-2.45	7.2-78.8	0.67-21.2	1.2-4.6	8-102	0.54-1.15	0.39-1.5	ND	4.3-11.4	0.4-1.3	0.6-1.6	ND	Current study
The Yangtze River from Dongting lake outlet to Shanghai section	0.39-4.7	10.1-854	ND-22.9	1.1-10.3	2.9-21.4	0.25-0.81	0.41-1.2	ND	8.4-16.5	0.8-18.5	0.7-1.96	ND	
Uangpu River	ND-1.98	6.3-145	5.7-42.7	3.4-6.4	22-60.6	1.8-3.3	1.0-1.6	ND	6.3-15.6	7.0-13.9	1.54-4.28	ND	
Taihu Lake in Gonghu Lake	1.3-4.1	28.0-197	9.27-110	0.68-5.07	16.6-24.4	0.94-2.15	0.79-1.42	ND	8.67-22.62	4.62-23.98	2.04-5.06	ND	
Jiaxing urban city	ND-1.21	7.58-115	3.02-4.05	3.06-4.61	28.4-33.9	1.29-2.26	0.79-1.82	ND	4.39-11.47	3.08-12.37	1.0-1.68	ND	
Songhua River	—	—	—	—	0.02-2.68	—	—	—	—	—	0.06-8.04	—	(Liu et al., 2007)
The Pearl river in Guangzhou section	—	—	ND-2.2	ND-4.1	0.85-13	ND-3.1	ND-0.57	ND-0.40	—	—	0.9-99	—	(So et al., 2007)
The Yangtze River in Chongqing section	—	—	0.3-0.32	0.22-0.33	23-35	ND	ND-0.043	ND	—	—	ND-0.39	—	
The Yangtze River in Yichang section	—	—	ND-0.19	0.074-0.11	4.1-5.3	ND-0.12	0.014-0.054	ND-0.081	—	—	0.29-0.82	—	
The Yangtze River in Shanghai section	—	—	0.39-5.3	0.55-9.2	22-260	0.48-10	0.11-3.8	ND-3.0	—	—	0.62-14.0	—	
Liao River	—	—	—	ND-23.3	ND-27.9	ND	ND	ND	ND	1.4-94.5	ND-6.6	ND	(Yang et al., 2011)
Hun River	—	—	2.12-11.3	0.56-4.0	2.68-9.13	0.78-1.55	ND	ND	—	—	0.40-3.32	—	(Sun et al., 2011)
Haihe River	—	—	2.2-42	1.3-9	4.4-42	ND-2.7	ND-0.15	ND-0.1	—	—	2.0-7.6	—	(Li et al., 2011)
Han River in Wuhan section	—	—	ND	ND	ND-256	ND-73.6	ND-94.9	ND-76.7	—	—	ND-88.9	—	(Wang et al., 2013)
Fen River in Taiyuan section	—	—	—	—	2.49-4.79	—	—	—	—	—	3.54-16.23	—	(Higashiguchi et al., 2013)

“ND” represents not detected; “—” means not analyzed.

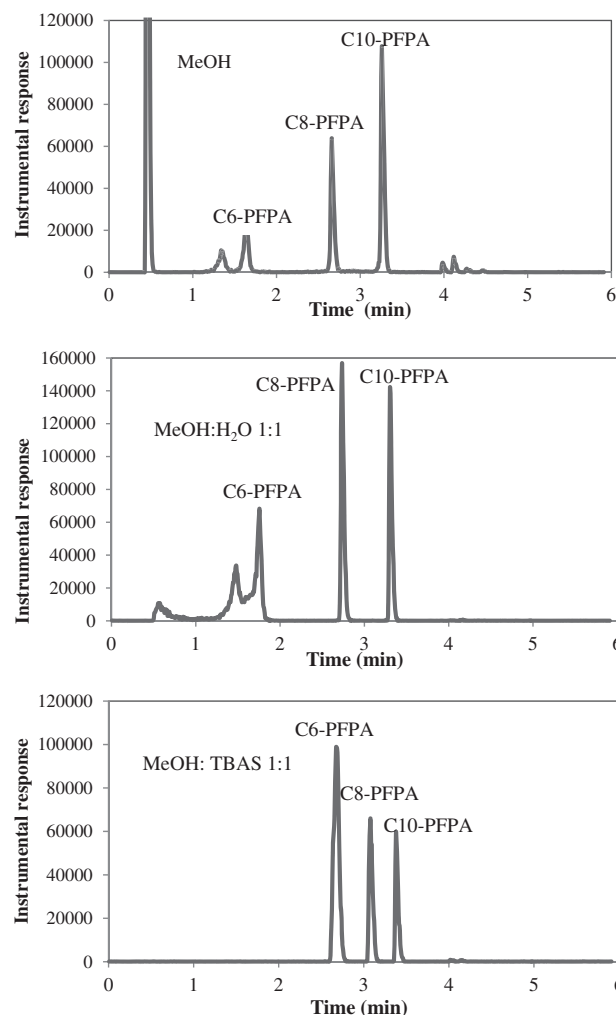
peak shape. The mobile phase consisted of 0.1%  $\text{NH}_4\text{OH}$  in water as the aqueous phase and pure methanol as the organic phase, which dramatically enhanced the sensitivity of PFPAs. Standard solutions of PFPAs, PFPiAs and diPAPs were prepared in three different solvent compositions (i.e., methanol:water 1:1, pure methanol, and methanol:25 mmol/L TBAS) for comparison. The results showed that the PFPAs standard solution prepared in methanol and 25 mmol/L TBAS at a 1:1 ratio provided high instrumental response and symmetric peak shape (Fig. 2). Further, the standard solutions composed of methanol/water (50/50) and pure methanol both produced high instrumental sensitivity and symmetric peak shape for PFPiAs and diPAPs. Since the solvent used in both PFCA and PFSA standard solutions was methanol/water (50/50), the same solvent composition was selected for PFPiA and diPAP analyses.

## 2.2. PFCAs and PFSA in surface water

Among the 15 PFCAs and PFSA analyzed, 10 compounds were detected in all water samples. None of the long-chain (C11 to C14) PFCAs or perfluorodecane sulfonate (PFDS) were detected in water samples. Perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS, perfluorohexanoate (PFHpA), PFOA, perfluorononanoate (PFNA) and perfluorodecanoate (PFDA) were detected in all water samples. Perfluorobutanoate (PFBA) was found in 70% of the water samples analyzed and perfluorohexanoate (PFHxA) was detected in almost all water samples except for CJ-2. The ratios of concentrations of short chain PFCAs (defined as carbon number  $\leq 7$ ) to that of PFOA and short chain PFSA (carbon number  $\leq 6$ ) to that of PFOS ranged from 1.5 to 86.2 and 3.1 to 22.6, respectively, suggesting that PFOA and PFOS were substituted by short-chain PFCAs and PFSA. The highest concentrations of PFBS (22.6 ng/L), PFHxS (24.0 ng/L) and PFOS (5.06 ng/L) were found in samples collected from Taihu lake (TH-8, TH-4, and TH-6, respectively).

The concentration distribution patterns of 11 PFCAs and 4 PFSA are shown in Fig. 3. The total concentration of 11 PFCAs and 4 PFSA (total PFASs) in the YRD showed a wide variation from 31 to 902 ng/L. The highest and lowest concentrations were detected in the Yangtze and Qiantang rivers, respectively. The mean concentration of total PFASs in the study areas decreased in the following order: Yangtze river (191 ng/L)  $\approx$  Taihu lake (189 ng/L)  $>$  Huangpu river (122 ng/L)  $\approx$  Qiantang river (120 ng/L)  $>$  Jiaying urban river (100 ng/L). The distribution pattern also showed a significant difference in the various study areas. In the Yangtze river, Jiaying urban river and Taihu lake, perfluoropentanoate (PFPeA) was the dominant congener, while PFOA was predominant in the Huangpu and Qiantang rivers. Although the dominant congeners varied in the study areas, the proportion of total PFCAs was more than 66% of the total PFASs.

The percentage of PFPeA showed a large variation in the Yangtze River; PFPeA percentage in the total PFASs of CJ-1 to CJ-12 (48.9%–94.7%) was much higher than that of CJ-13 and -14 (16.9% and 20.7%, respectively). These differences may be due to the location of CJ-13 and CJ-14 being in the estuary, where water is diluted by coastal seawater. Indeed, the concentrations of PFCAs and PFSA in seawater are usually lower than 20 ng/L (So et al., 2004). Conversely, the CJ-1 sample in which high total

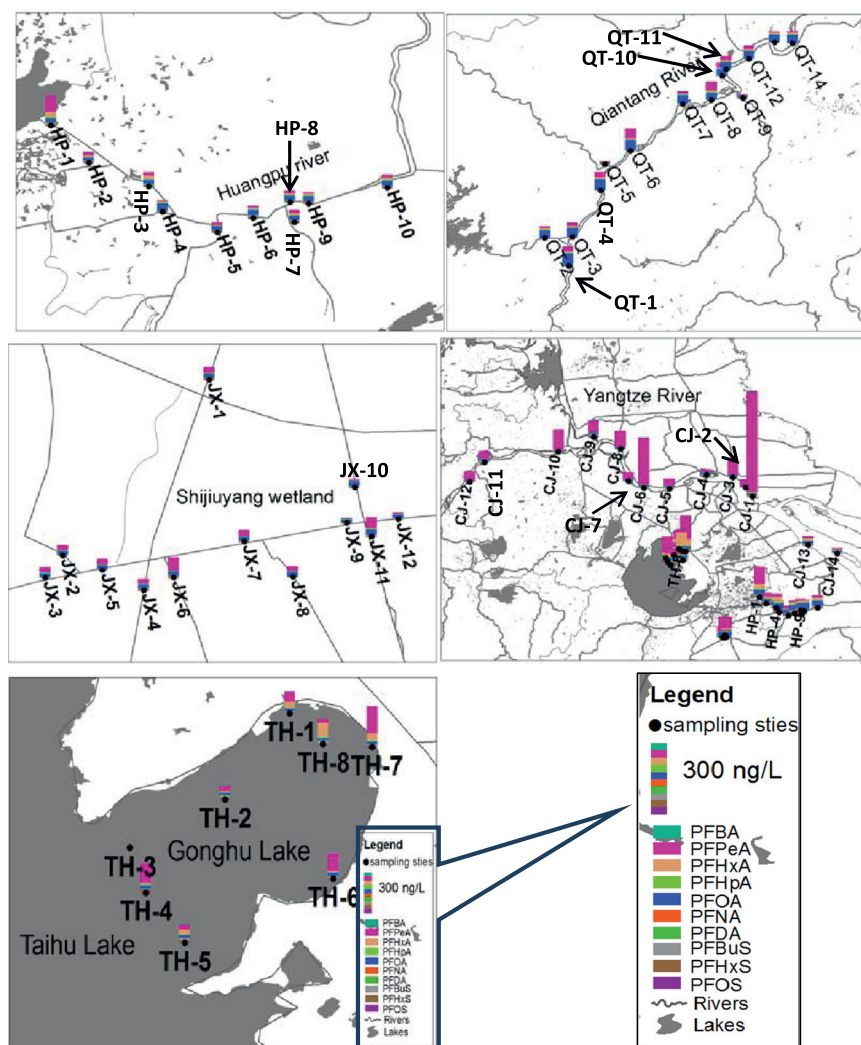


**Fig. 2 – Effect of solvent composition on PFPAs standard solution on chromatographic separation and instrumental response.** PFPAs: perfluoroalkyl phosphonic acids; MeOH: methanol; TBAS: tetrabutylammonium hydrogen sulfate; C6-PFPA: perfluorohexyl phosphonic acid; C8-PFPA: perfluorooctyl phosphonic acid; C10-PFPA: perfluorodecyl phosphonic acid.

PFSA were detected, was retrieved from an area near an urban community and industrial park including printing, dyeing, polymer, metal, photoelectric material, mechanical, and auto-parts manufacturing, which may produce wastewater with high total PFASs.

In Jiaying urban river samples, PFPeA accounted for 44%–64% of total PFASs. However, JX-9, JX-10 and JX-12 showed different PFCA and PFSA profiles from the remaining JX samples, with the PFPeA concentration contributing to less than 15% of total PFASs, which suggests different pollution sources from other JX samples. Sample JX-1 was collected upriver of the SHIJIUYANG wetland system, which is the largest urban drinking water source treatment system in China. Sample JX-7 was collected in the effluent of the wetland system. The total PFASs of JX-7 (102 ng/L) was slightly lower than that of JX-1 (114 ng/L), indicating that SHIJIUYANG wetland system is not able to significantly remove PFCAs and PFSA.





**Fig. 3 – PFAS level in Yangtze River, Qiantang River, Huangpu River, Taihu Lake and Jiaying urban river (ng/L). PFAS:** perfluoroalkyl substances; **PFBA:** perfluorobutanoic acid; **PFPeA:** perfluoropentanoic acid; **PFHxA:** perfluorohexanoic acid; **PFHpA:** perfluoroheptanoic acid; **PFOA:** perfluorooctanoic acid; **PFNA:** perfluorononanoic acid; **PFDA:** perfluorodecanoic acid; **PFBS:** perfluorobutanesulfonate; **PFHxS:** perfluorohexanesulfonate; **PFOS:** perfluorooctanesulfonate.

In the seven samples collected from Taihu, the highest total PFASs concentrations were found in TH-7 (308 ng/L), followed by TH-4 (215 ng/L) and TH-8 (196 ng/L). Samples TH-7 and TH-8 were collected near the entrance of the river into the lake, which was shown to be highly polluted in an earlier study (Shu, 2011).

The highest concentration of total PFASs in the Huangpu river was detected in HP-1 (265 ng/L), which was twice higher than those in HP-2 to HP-10 (92–123 ng/L). HP-1 was collected downstream of Dianshan lake, which is mainly affected by catering and entertainment activities in the Dianshan lake and its surroundings. Samples HP-2, HP-4, HP-5, and HP-7 were collected from different branches, where dilution may play an important role, resulting in relatively lower PFASs concentrations. Indeed, the PFCAs and PFSAs profiles in HP-1 were different from those in HP-2 to HP-10, indicating different contaminant sources.

In the Qiantang river, PFOA was the dominant congener and total PFCAs accounted for 68%–97% of the total PFASs,

where the total PFASs were higher than 100 ng/L, except for QT-5 and QT-9 (31.1 and 36.9 ng/L, respectively). Relatively low concentrations of PFCAs in QT-5 and QT-9 (23.6 and 25.3 ng/L, respectively) suggest that the river branches did not aggravate the PFCA and PFSA pollution of the mainstream.

### 2.3. Relationship between PFCAs and PFSAs in surface water

Regression analyses were conducted to examine the correlations among pollutant concentrations in surface water from each of the study areas (Appendix A. Tables S1–S5). Significant ( $p < 0.05$ ) correlations were found among various compounds, suggesting a common source. Hierarchical cluster analysis was conducted with squared Euclidean distance to investigate the relationship between the individual PFASs concentrations in the surface waters of each river or lake. Prior to cluster analysis, each PFAS concentration was normalized by the total PFASs. The Qiantang samples were classified into five



groups (A-E); while Yangtze, Huangpu, and Jiaying urban river samples were classified into two or three groups (Appendix A, Figs. S1–S5). Thus, samples were classified according to the total PFASs. For example (Appendix A, Fig. S4), total PFAS contents of groups A and B were lower than 129 ng/L, those of groups C and D were approximately 160 ng/L and 180 ng/L, respectively, and that of group E, composed of QT-5 and -9, was approximately 30 ng/L. The percentage of PFOA in group B was obviously higher than that in group A. The relatively lower total PFASs concentration in QT-5 and -9 indicated that both tributaries of Qiantang river did not show increased total PFASs pollution. As shown in Fig. S3 (Appendix A), group A includes samples JX-1 to -5, -7, -8, and -11, group B includes JX-9, -10, and -12, and group C includes only JX-6. Group A showed similar PFCA and PFSA profiles and the total PFASs ranged from 92 to 114 ng/L, suggesting that the samples share common sources for these compounds. The total PFASs (62–74 ng/L) and PFPeA (7.6–11 ng/L) concentrations were much lower in group B than in other groups. Finally, group C had much higher concentrations of PFPeA and total PFASs, suggesting different contamination sources from groups A and B.

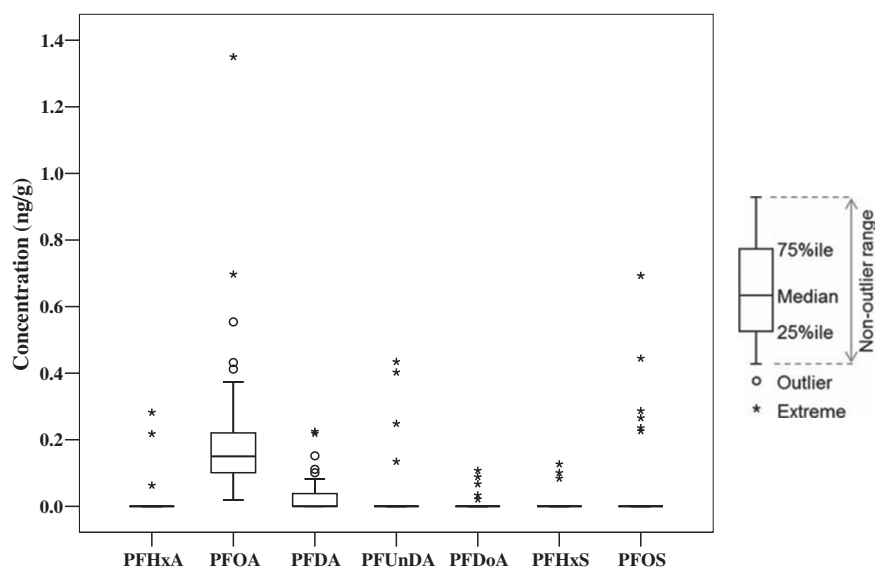
## 2.4. PFCAs and PFASs in sediment

Among the 15 PFCAs and PFASs analyzed, five PFCAs and two PFASs were detected in sediment samples. The highest detection frequencies (100%) as well as the highest concentrations in sediment samples were for PFOA (0.02–1.35 ng/g). The detection frequency of seven PFCAs and PFASs increased in the following order: PFHxA = PFHxS (6.4%) < perfluoroundecanoate (PFUnDA, 8.5%) < perfluorododecanoate (PFDoA, 10.6%) < PFOS (12.8%) < PFDA (38.3%) < PFOA (100%). The arithmetic mean concentrations of seven detectable PFCAs and PFASs increased from PFHxS (0.0066 ng/g, ranging from ND to 0.13 ng/g)  $\approx$  PFDoA (0.0067 ng/g, ND to 0.11 ng/g) < PFHxA (0.012 ng/g, ND to 0.028 ng/g) < PFUnDA (0.026 ng/g, ND to 0.43 ng/g) < PFDA

(0.030 ng/g, ND to 0.22 ng/g) < PFOA (0.21 ng/g, 0.02–1.35 ng/g) (Fig. 4). The observed low concentrations and detection frequencies for all PFCAs and PFASs except PFOA were attributed to their low affinity for sediment, which can be explained by their low organic carbon-normalized distribution coefficient ( $K_{oc}$ ) values (Higgins and Luthy, 2006; Kwadijk et al., 2010; Zareitalabad et al., 2013). Although PFBS, PFHxS, PFPeA, PFHxA and PFHpA were frequently detected in surface water, even at times at a higher concentration than PFOA and PFOS, the lower detection frequency and concentration in sediment indicate that these substitutions are due to solubility.

## 2.5. Distribution of PFCAs and PFASs between water and sediment

The partitioning of organic pollutants between water and sediment is one of the most important factors affecting their environmental behavior and fate. The PFCAs and PFASs distribution between sediment and water is governed by their physical and chemical properties as well as environmental characteristics such as the sediment organic carbon content, pH, ionic strength, and salinity (Higgins and Luthy, 2006; Pan and You, 2010). It was reported that the measured distribution coefficients ( $K_d$ ) of anionic perfluorochemical surfactants in sediment increased with decreasing pH, with a rate of change of approximately 0.37 log unit per unit pH (Higgins and Luthy, 2006). In the current study, significant relationships were found ( $p < 0.05$ ) between the sediment-water distribution coefficient of PFOA and TOC of Jiaying sediment (Pearson correlation coefficient, 0.643). However, significant relationships between the sediment-water distribution coefficient of PFOA and TOC were not observed in other areas of this study, suggesting that other influences on the sediment-water distribution, such as pH, ionic strength, and structure of organic carbon may be also in effect. Higgins and Luthy (2006) reported that  $\log K_d$  of anionic perfluorochemical surfactants in sediment increased with decreasing pH, with a rate of change of approximately 0.37 log



**Fig. 4** – Box-whisker plot of concentrations of PFCAs and PFASs in sediment samples. PFCAs: Perfluoroalkyl carboxylic acids; PFASs: perfluoroalkane sulfonic acids; PFUnDA: perfluoroundecanoic acid; PFDoA: perfluorododecanoic acid.

unit per unit pH. In the present study, the pH value of Jiaying surface water showed a narrow range over 7.35–7.60, while pH values of Taihu lake, Yangtze river, Qiantang river and Huangpu river varied from 8.14 to 9.20, 8.0 to 9.16, 7.39 to 9.19 and 7.38 to 8.39, respectively, in which the variations are more than one pH unit. So, it is likely that the  $K_d$  values of PFOA from Taihu lake, Yangtze river, Qiantang river and Huangpu river are also affected by pH value in addition to TOC content.  $K_{oc}$  is the most commonly used parameter in the evaluation of organic pollutants partitioning in the water environment.  $K_{oc}$  was calculated using the following equation:

$$K_{oc} = (C_s/C_w)/f_{oc}$$

where  $C_s$  is the concentration of PFASs in the entire sediment based on dry weight (ng/g);  $C_w$  is the concentration of PFASs in water at equilibrium (ng/mL); and  $f_{oc}$  is the organic carbon fraction in the sediment (%). Here, the  $\log K_{oc}$  value of PFOA in Jiaying ranged from 1.69 to 2.57, with an average value of 2.13; whereas, the  $\log K_{oc}$  value of PFDA varied from 2.90 to 3.92 with an average value of 3.26. The difference between  $\log K_{oc}$  of PFDA and PFOA suggests that each  $-CF_2$  group contributes 0.5–0.6 log units to the  $\log K_{oc}$  value, which is consistent with the results of a previous study (Shu, 2011). Paradoxically, PFNA could not be detected in the sediment of Jiaying river, even though the PFNA concentration in the Jiaying water sample is similar to that of PFDA. This could be due to the hypothetical  $\log K_{oc}$  value of PFNA being approximately 3.2, which would lead to a PFNA concentration in sediment of approximately 0.02 ng/g, considerably lower than the limit of detection.

## 2.6. Comparison of PFASs concentrations in water samples from freshwater rivers

The YRD economic zone is one of the most rapidly developing areas in China. Therefore, the contaminant condition of YRD has drawn the attention of environmental researchers. Surface water and sediment samples collected from the Gonghu region of Taihu lake in 2010 showed total PFASs content of approximately 250 and 1.5 ng/g, respectively. The dominant congeners in surface water and sediment were PFOA and PFBA, respectively, and no PFSAs were detected in surface water except PFOS (Lu, 2011). The total PFASs in surface water in the current study were similar to the values reported by Lu (2011), indicating that the PFCA and PFSA contamination has not ameliorated since 2010. However, the distribution profile has changed, wherein PFPeA is now the dominant congener along with PFBS; additionally, PFHxS was detected at a concentration higher than that of PFOS. Thus, these results also reflect the trend of substitution of long-chain PFCAs and PFSAs by their short-chain counterparts.

In a previous work, Hangzhou city environmental monitoring center assessed PFCAs and PFSAs contamination characteristics of Qiantang river surface water collected in July 2014 (wet season) and January 2015 (dry season) (Zhang et al., 2015). The surface water samples in the present study were collected in April 2015 (normal season). In most areas of China, the ‘wet season’ usually lasts from May to September, with abundant precipitation, and the ‘dry season’ lasts from December to

February, with scarce rainfall. The ‘normal season’ occurs during the in-between months and during this period, a river is at its normal level. The water level varies greatly during the dry, wet and normal seasons, resulting in a major variation in PFCAs and PFSAs contamination levels. Therefore, it is necessary to evaluate the PFCAs and PFSAs contamination according to the water level. A comparison of the PFCA and PFSA contamination level of Qiantang river surface water between the three seasons (current study versus Zhang, 2015) shows that the total PFASs were highest in the dry season and lowest in the wet season (Fig. 5), indicating a negative correlation with water level. Further, PFOA was found to be the dominant congener in both studies. However, the contribution of PFOA to the total PFASs was lower in the present study; conversely, the detection frequencies for PFBS, PFHxS, PFNA and PFDA were much higher. Table 3 shows the comparison of PFCAs and PFSAs in water samples from freshwater rivers in previous studies. It is obvious that the detection rate and concentrations of short-chain PFCAs and PFSAs in the present study are much higher. However, the PFOA and PFOS levels are not significantly higher herein.

## 2.7. PFPAAs, PFPIAs, and diPAPs in surface and sediment

PFPAAs and PFPIAs were not detected in any water and sediment samples; 6:2 diPAP was observed in water samples from TH-1, TH-6, JX-1, CJ-7, and CJ-12 at concentrations ranging from 0.102 to 0.278 ng/L, while 8:2 diPAP was detected only in TH-1 (0.916 ng/L) and TH-5 (0.446 ng/L), at 2 to 3 orders of magnitude lower than those of PFOA.

Similarly, only 6:2 and 8:2 diPAPs were observed in several sediments of Jiaying urban river, Taihu lake and Huangpu river; indeed, 6:2 diPAP and 8:2 diPAP were detected in five and four sediment samples out of a total of 47 samples, respectively. JX-6 showed the highest diPAP levels at 1.44 ng/g for 6:2 diPAP and 4.05 ng/g for 8:2 diPAP (Fig. 6). Overall, the 8:2 diPAP concentration (0.235–4.05 ng/g) was generally higher than that of 6:2 diPAP (0.088–1.44 ng/g). Although only low levels of diPAPs were detected, it is known that diPAPs are reactive and will degrade to PFCAs, so further work should be performed to identify their environmental cycle.

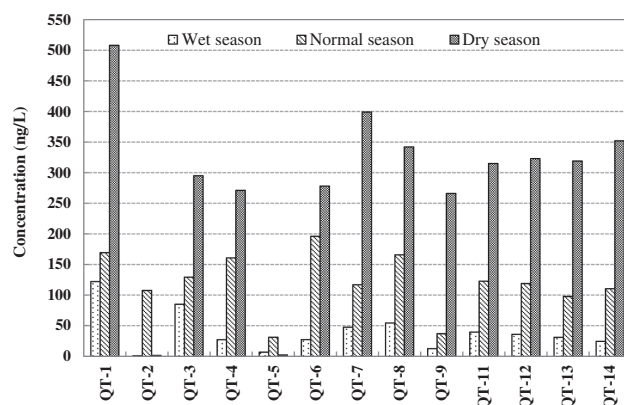


Fig. 5 – Comparison of PFAS levels of current study with the previous study.

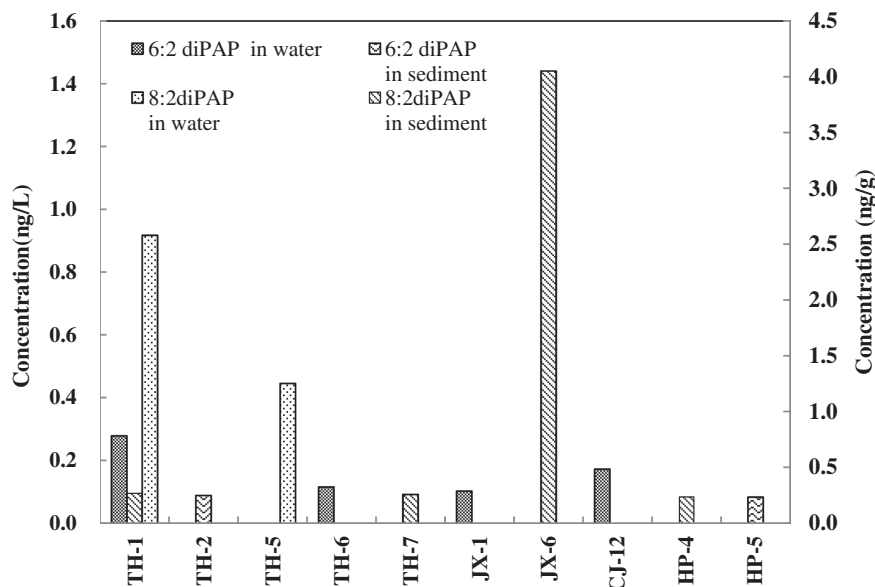


Fig. 6 – DiPAPs concentrations in surface water and sediment. DiPAPs: polyfluoroalkyl phosphoric acid diesters; 6:2 diPAP: 6:2 fluorotelomer phosphate diester; 8:2 diPAP: 8:2 fluorotelomer phosphate diester.

### 3. Conclusions

Herein, PFCA, PFSA, PFPA, PFPiA, and diPAP contamination levels in drinking water sources of major Chinese cities were studied. The detection frequency and concentration of PFCAs and PFSAs in surface water were much higher than those in sediment. The mean concentrations of total PFCAs and PFSAs decreased in the following order: Yangtze river (191 ng/L)  $\approx$  Taihu lake (189 ng/L) > Huangpu river (122 ng/L)  $\approx$  Qiantang river (120 ng/L) > Jiaying urban river (100 ng/L). Significant ( $p < 0.05$ ) correlations among many of the compounds were found in all the areas, suggesting a common source for these compounds. Only PFOA was detected in all sediment samples, at concentrations varying from 0.02 to 1.35 ng/g. A positive relationship between the  $\log K_{oc}$  of PFOA and the sediment TOC in Jiaying urban river was observed. Only diPAPs were detected in the seven samples, including surface water and sediment. To the best of our knowledge, this is the first report on PFPAs, PFPiAs and diPAPs contaminant levels in drinking water sources in the YRD region. US EPA has established both PFOA and PFOS health advisory levels at 70 parts per trillion. When both PFOA and PFOS are found in drinking water, their combined concentrations should be compared with the health advisory level (EPA, 2016). In current study, the combined amounts of PFOA and PFOS from CJ-1, -3, -4 and -8 are higher than the advisory limit of 70 parts per trillion, which indicated long-term consumption the water in these areas would pose a risk on human health. However, the present study shows that the contamination of short-chain PFCAs and PFSAs is more common and more serious. Furthermore, there was not enough evidence to prove the effects of the long-term consumption of short-chain PFCAs and PFSAs contaminated water on humans and animals. Further studies should be performed to evaluate the health risks of short-chain PFCAs and PFSAs on humans and animals.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jes.2017.09.015>.

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