

# Spatial Distribution of Perfluoroalkyl Substances in Surface Sediments of Five Major Rivers in China

Chang-Gui Pan · Guang-Guo Ying ·  
Jian-Liang Zhao · You-Sheng Liu · Shuang-Shuang Liu ·  
Jun Du · Rai S. Kookana

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**Abstract** Perfluoroalkyl substances (PFASs) have received great attention from the public and scientific community due to their potential adverse impacts on the ecosystem and human health. We investigated the occurrence and distribution of 16 PFASs from 2 classes of PFASs—perfluoroalkyl carboxylic acids and perfluoroalkane sulfonic acids—in the archived surface sediments of five major rivers (Yellow River, Hai River, Liao River, Zhujiang River, and Dongjiang River) in northern and southern China. The study was also performed during the wet and dry seasons. Perfluorooctanoic acid and perfluorooctane sulfonic acid were the most frequently detected (detection frequency = 100 and 63 %, respectively) in the sediments of the five rivers; the concentrations ranged from 0.08 to 0.99 ng/g dry weight (dw) and were lower than the limit of detection (<LOD), which is 3.89 ng/g dw for both. Perfluorodecanoic acid and perfluoroundecanoic acid were moderately detected (detection frequency = 42 and 44 %, respectively) with concentrations ranging from less than their limit of detection (<LOD) to 0.69 ng/g dw and <LOD to 0.22 ng/g dw, whereas 12 other target analytes were lower than their limit of quantification at most of the sampling sites. Greater concentrations of the PFASs were found at those sites located in urban areas compared with rural areas. Sediment

organic content was found to be an important factor influencing the distribution of PFASs in the riverine environment. The results provided first-hand national data of PFASs in the sediments of major rivers in China.

Due to their unique physicochemical characteristics—such as high surface activity, thermal and acid resistance, and water and oil repellency—perfluoroalkyl substances (PFASs), especially perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFASAs), and/or their precursors (i.e., alcohols, acrylates, amides), have been extensively employed in industrial and consumer applications, for example, in pesticide formulations, surfactant (Key et al. 1997), textiles, carpets, paper, food packaging (Giesy and Kannan 2002), grease, lubricating oils, polishes, mist suppressants (Lewandowski et al. 2006), and fire-fighting foams (Moody and Field 2000). PFASs in products may be released into the environment through discharge of wastewaters (Schultz et al. 2006; Sun et al. 2011; Lin et al. 2010) and disposal of wastes containing these compounds. Because of the high energy carbo-fluorine covalent bond, PFCAs and PFASAs have shown high persistence against the typical environmental degradation processes (Kissa 2001) as well as high bioaccumulation ability (Martin et al. 2003; Morikawa et al. 2006), potential adverse effect (Fei et al. 2007; Fletcher et al. 2013; Kudo and Kawashima 2003), and long-range atmosphere transport indirectly by abiotic and/or biotic degradation of precursor chemicals (Stock et al. 2007) and ocean currents directly (Yamashita et al. 2008). Several previous studies have not only found PFASs in environmental media, e.g., air (Li et al. 2011b; Schlummer et al. 2013; Shoeib et al. 2006), water (Boulanger et al. 2004; Hansen et al. 2002; Hong et al. 2013), sediment (Bao et al. 2009; Zhao et al. 2013), and biota (Giesy and Kannan 2001; Tao et al. 2006; Hlouskova

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C.-G. Pan · G.-G. Ying (✉) · J.-L. Zhao · Y.-S. Liu · S.-S. Liu  
State Key Laboratory of Organic Geochemistry, Guangzhou  
Institute of Geochemistry, Chinese Academy of Sciences,  
Guangzhou 510640, People's Republic of China  
e-mail: guang-guo.ying@gig.ac.cn; guangguo.ying@gmail.com

J. Du · R. S. Kookana  
CSIRO Land and Water, PMB 2, Glen Osmond, SA 5064,  
Australia

et al. 2013) but also in human blood and serum (Ji et al. 2012; Kannan et al. 2004; Toms et al. 2009; Zhang et al. 2010). In general, the concentrations of individual PFAS in environmental matrices (water, sediment, soil) range from levels of picograms per gram to nanograms per gram (Boulanger et al. 2004; Hansen et al. 2002; Bao et al. 2009, 2010; Zhao et al. 2013; Strynar et al. 2012).

Sediment phase has been regarded as a sink and also a secondary source for PFASs because PFASs can undergo desorption process and release back to the water phase (You et al. 2010), and this has a significant impact on their distribution, fate, bioaccumulation, and biological effects (Martin et al. 2004; Prevedouros et al. 2006). Their distribution in aquatic sediments can reflect the contamination profiles in a region. Some previous studies have reported detection of PFASs in sediments, e.g.,  $\leq 536.7$  ng/g dw for perfluorooctane sulfonic acid (PFOS) in Yangtze River estuarine sediment (Pan and You 2010), which is lower than the limit of detection (<LOD) to 1.6 ng/g dw in Laizhou Bay sediment (Zhao et al. 2013) and 4.0–4.6 ng/g dw in Orge River sediment (Labadie and Chevreuil 2011). Greater concentrations of PFASs have been reported in surface sediments than in deep sediment layers suggesting increasing contamination of PFASs in recent years (Ahrens et al. 2009; Bao et al. 2009).

As one of the largest industrial country in the world, China houses several fluoro manufactures, which makes China to be almost the only production country for PFOS since the 3 M Company, the largest manufacturer of PFOS, announced it would phase out the production of PFOS in 2000 (Zhang et al. 2012). To have a systematic understanding of PFAS pollution, three rivers (Yellow River, Hai River, and Liao River) in north China and two rivers (Zhujiang River and Dongjiang River) in south China were selected to investigate PFASs levels and distribution in Chinese river sediments. The Yellow River is the second longest river in China, which flows from the west to the Bohai Bay, and is known for its high silt and sand content. The Hai River flows to the Bohai Bay from Beijing through another large industrial city Tianjin with more than ten million inhabitants. The Liao River flows from Qilaotu Mountain to the Bohai Bay, which passes through some industrial cities (Shenyang, Benxi, and Anshan) in north-east China. The Zhujiang River is the third longest river in China, which flows from Yunnan to the South China Sea at Guangzhou. The Dongjiang River flows to the South China Sea from Jiangxi through the industrial cities of Huizhou and Dongguan.

The objective of this study was to investigate the levels of PFASs in archived sediments from five major representative rivers (Liao River, Hai River, Yellow River, Zhujiang River, and Dongjiang River) in north and south

China and to assess the spatial variations of these PFASs in the five rivers. The results from this study will provide useful information of PFASs contamination in Chinese riverine environments.

## Materials and Methods

### Chemicals and Reagents

Sixteen PFASs (11 PFCAs, 5 PFASs) were selected for this investigation. Full chemical name, acronym, and formula for each PFAS are listed in Table 1. Purities of all of the analytical standards were  $\geq 95$  %. Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), and perfluorohexanoic acid (PFH<sub>x</sub>A) were purchased from J&K Company (China), Acros Organics (Geel, Belgium), and Tokyo Chemical Industries (Portland, Oregon, USA), respectively. Perfluorooctanoic acid (PFOA) and PFOS were obtained from AccuStandard (New Haven, Connecticut, USA). Perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFD<sub>O</sub>DA), and perfluorotetradecanoic acid (PFTeDA) were acquired from Alfa Aesar (Ward Hill, Massachusetts, USA). Perfluoroundecanoic acid (PFUnDA), perfluorotridecanoic acid (PFTrDA), perfluorobutane sulfonic acid (PFBS), and perfluorohexane sulfonic acid (PFH<sub>x</sub>S) were obtained from Sigma-Aldrich (St. Louis, Missouri, USA). Perfluoroheptane sulfonic acid (PFHpS), perfluorodecane sulfonic acid (PFDS), MPFH<sub>x</sub>A (<sup>13</sup>C<sub>2</sub>-PFH<sub>x</sub>A), MPFOA (<sup>13</sup>C<sub>4</sub>-PFOA), MPFNA (<sup>13</sup>C<sub>5</sub>-PFNA), MPFDA (<sup>13</sup>C<sub>2</sub>-PFDA), MPFH<sub>x</sub>S (<sup>18</sup>O<sub>2</sub>-PFH<sub>x</sub>S), and MPFOS (<sup>13</sup>C<sub>4</sub>-PFOS) were bought from Wellington Laboratories (Guelph, Ontario, Canada). Six internal standards were the corresponding carbo-13 (<sup>13</sup>C) or 18-oxygen (<sup>18</sup>O<sub>2</sub>) mass-labeled native standards. Ammonium acetate [liquid chromatography (LC)-mass spectrometry (MS) grade, >99 %], methyl *tert*-butyl ether [MTBE; high-performance liquid chromatography (HPLC) grade], sodium carbonate anhydrous (Na<sub>2</sub>CO<sub>3</sub>), and tetrabutyl ammonium hydrogen sulfate (TBAHS, HPLC grade) were all purchased from CNW (Dusseldorf, Germany). Ammonium hydroxide (10 %) and acetic acid were bought from Fluka (Germany). HPLC-grade methanol was purchased from Merck Corporation (Darmstadt, Germany). Ultrapure water was supplied by a Milli-Q system from Millipore (Watford, United Kingdom). Individual stock solutions of the target analytes and internal standards were prepared in methanol and stored in polypropylene (PP) bottles at  $-18$  °C. Composite working solutions at the desired concentrations were made by appropriate dilution of the individual stock solutions.

**Table 1** Analyte formula, acronym, and optimum LC–MS/MS parameters for MRM acquisition conditions of individual PFASs

Compound	Acronym	Formula	MS/MS mass transition	Fragmentor (V)	Collision energy (V)
Perfluorobutanoic acid	PFBA	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>2</sub> COOH	213–168.8 <sup>a</sup>	65	5
Perfluoropentanoic acid	PFPeA	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>3</sub> COOH	263–218.8 <sup>a</sup>	65	1
Perfluorohexanoic acid	PFH <sub>X</sub> A	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> COOH	313–268.8 <sup>a</sup> /118.9 <sup>b</sup>	70	1/13
Perfluoroheptanoic acid	PFHpA	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> COOH	363–318.8 <sup>a</sup> /168.8 <sup>b</sup>	70	1/9
Perfluorooctanoic acid	PFOA	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>6</sub> COOH	413–368.7 <sup>a</sup> /168.9 <sup>b</sup>	80	1/9
Perfluorononanoic acid	PFNA	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>7</sub> COOH	463–418.7 <sup>a</sup> /218.8 <sup>b</sup>	90	1/9
Perfluorodecanoic acid	PFDA	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>8</sub> COOH	513–468.7 <sup>a</sup> /218.8 <sup>b</sup>	85	5/13
Perfluoroundecanoic acid	PFUnDA	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>9</sub> COOH	563–518.7 <sup>a</sup> /268.8 <sup>b</sup>	90	5/13
Perfluorododecanoic acid	PFDOA	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>10</sub> COOH	613–568.7 <sup>a</sup> /168.9 <sup>b</sup>	105	5/25
Perfluorotridecanoic acid	PFTTrDA	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>11</sub> COOH	663–618.7 <sup>a</sup> /168.9 <sup>b</sup>	110	5/25
Perfluorotetradecanoic acid	PFTeDA	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>12</sub> COOH	713–668.7 <sup>a</sup> /218.9 <sup>b</sup>	105	5/21
Perfluorobutane sulfonic acid	PFBS	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H	299–79.9 <sup>a</sup> /98.9 <sup>b</sup>	145	41/29
Perfluorohexane sulfonic acid	PFH <sub>X</sub> S	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> SO <sub>3</sub> H	398.9–79.9 <sup>a</sup> /98.9 <sup>b</sup>	165	53/37
Perfluorooctane sulfonic acid	PFOS	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>7</sub> SO <sub>3</sub> H	498.9–79.9 <sup>a</sup> /98.9 <sup>b</sup>	190	69/45
Perfluoroheptane sulfonic acid	PFHpS	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>6</sub> SO <sub>3</sub> H	448.9–79.9 <sup>a</sup> /98.9 <sup>b</sup>	180	61/41
Perfluorodecane sulfonic acid	PFDS	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>9</sub> SO <sub>3</sub> H	598.9–79.9 <sup>a</sup> /98.9 <sup>b</sup>	235	77/57
Perfluoro[1,2- <sup>13</sup> C <sub>2</sub> ]hexanoic acid (IS <sup>c</sup> )	MPFH <sub>X</sub> A		315–269.8 <sup>a</sup> /119.9 <sup>b</sup>	70	1/13
Perfluoro[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octanoic acid (IS <sup>c</sup> )	MPFOA		417–371.7 <sup>a</sup> /171.9 <sup>b</sup>	95	1/9
Perfluoro[1,2,3,4,5- <sup>13</sup> C <sub>5</sub> ]nonanoic acid (IS <sup>c</sup> )	MPFNA		468–422.7 <sup>a</sup> /218.8 <sup>b</sup>	95	1/9
Perfluoro[1,2- <sup>13</sup> C <sub>2</sub> ]decanoic acid (IS <sup>c</sup> )	MPFDA		515–469.7 <sup>a</sup> /269.9 <sup>b</sup>	90	5/9
Perfluoro[ <sup>18</sup> O <sub>2</sub> ]hexane sulfonic acid (IS <sup>c</sup> )	MPFH <sub>X</sub> S		402.9–83.9 <sup>a</sup> /102.9 <sup>b</sup>	145	45/37
Perfluoro[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octane sulfonic acid (IS <sup>c</sup> )	MPFOS		502.9–79.9 <sup>a</sup> /98.9 <sup>b</sup>	205	65/45

<sup>a</sup> Product ion used for quantification

<sup>b</sup> Product ion used for identification

<sup>c</sup> Internal standard

### Sample Collection and Sample Pretreatment

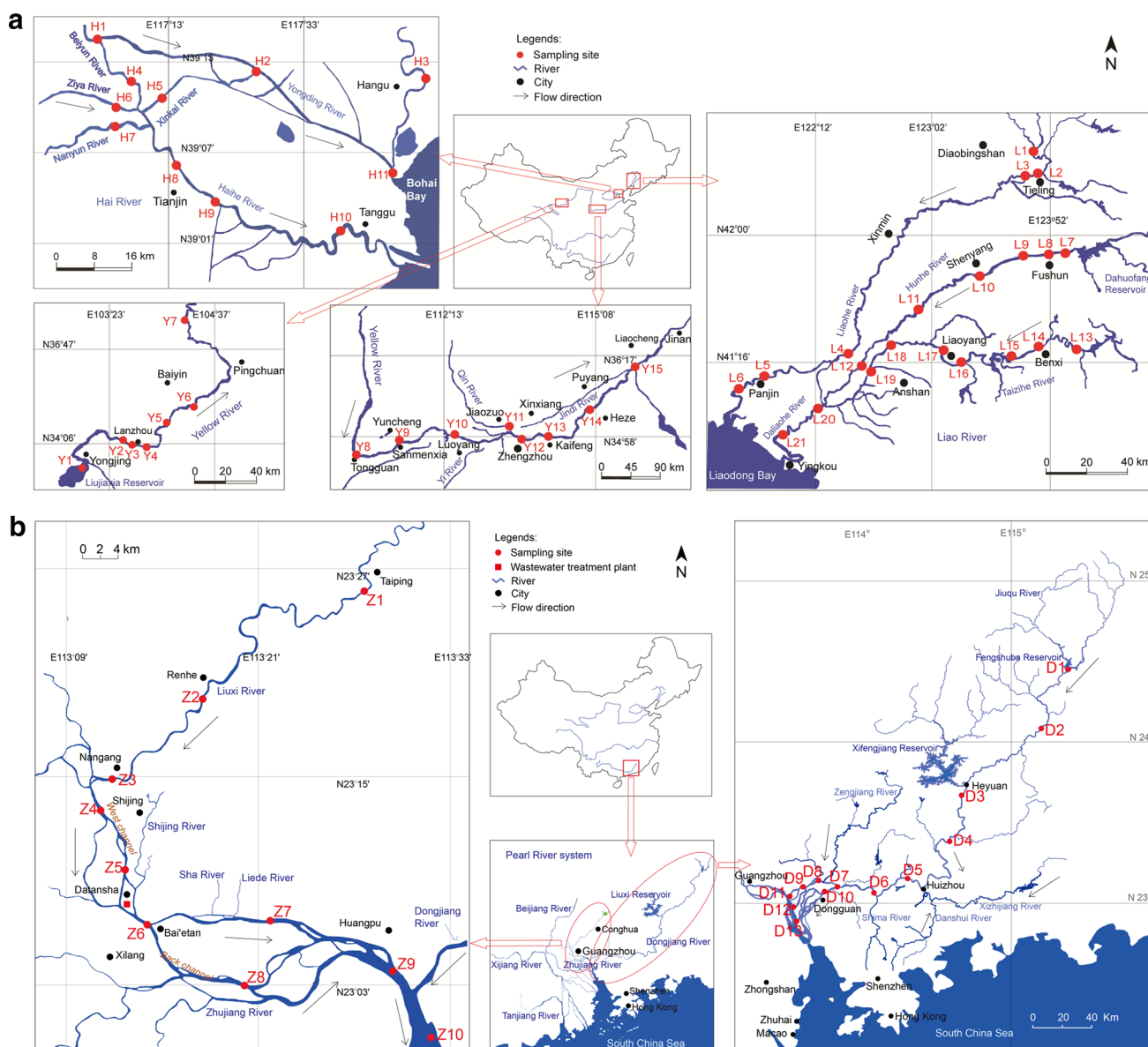
The archived sediment samples used in this study were collected from the Yellow River, Hai River, Liao River, Zhujiang River, and Dongjiang River during the wet and dry seasons from the year 2007 to 2009 (Fig. 1a, b). Sites Y1 to Y15 were located in the Yellow River, sites H1 to H10 in the Hai River, sites L1 to L21 in the Liao River, sites D1 to D13 in the Dongjiang River, and sites Z1 to Z10 in the Zhujiang River. Detailed information of the five river systems being studied (e.g., stem length, catchment size, specified water area, population, wastewater, and gross domestic product) is listed in Supplementary Table S1, whereas information about location, sampling time, and river flow of the sampling sites are described in Table S2.

The surficial sediment samples (approximately 0–5 cm) were collected using a core sampler and stored in 50-mL PP tubes, then freeze-dried, homogenized, passed through a 60-mesh standard sieve, and finally stored in a freezer at –18 °C until extraction. Total organic carbon (TOC) fraction of each sediment sample was analyzed by a LECO C230 carbon analyzer after removal of carbonates with

hydrochloric acid, and particle size distribution of the sediment was determined by using the pipette method adapted from Beuselinck et al. (1998). The sediment properties, including pH, particle size distribution, and sediment organic carbon content (TOC), are listed in Tables S3–S6.

### Sample Extraction

PFASs in sediments were extracted by the ion-pairing liquid-extraction method previously described by Hansen et al. (2001). Three replicate sediment samples from each site were used for the extraction. Briefly, 2 g of sediment was weighed into a 50-mL PP tube followed by addition of 100 µL of 50 ng/mL internal standard mixture (MPFH<sub>X</sub>A, MPFOA, MPFNA, MPFDA, MPFH<sub>X</sub>S, and MPFOS). Then the sample was mixed with 2 mL of high-purity Milli-Q water by vortexing for 2 min, then 2 mL of 0.25 M Na<sub>2</sub>CO<sub>3</sub> and 1 mL of 0.5 M TBAHS solutions were added for extraction by vortexing for 5 min followed by addition of 5 mL of MTBE; finally, the sample tube was vigorously shaken for 20 min. The organic and aqueous layers were



**Fig. 1** Sampling location maps for the five rivers. **a** Map showing sampling sites in the Liao River, Hai River, and Yellow River in north China. Sites L1–L21 are located in the Liao River; sites Y1–Y15 are located in the Yellow River; and sites H1–H11 are located in the Hai

River. **b** Map showing sampling sites in the Zhujiang River and Dongjiang River in south China. Sites Z1 to Z10 are located in the Zhujiang River, and sites D1 to D13 are located in the Dongjiang River

separated by centrifugation at  $2,259\times g$  for 30 min, and then MTBE was transferred into another 10-mL PP tube. Another 5 mL of MTBE was added into the remnant aqueous mixture again, followed by shaking and centrifuging with the previously described conditions, and the supernatant was combined with the first portion in the 10-mL PP tube. The MTBE extract was blown down to dryness under a gentle stream of nitrogen and then reconstituted in 500  $\mu\text{L}$  of methanol. The final extract was filtered through a 0.22- $\mu\text{m}$  nylon filter into a 1-mL PP snap-top vial with a polyethylene cap and stored at  $-18^\circ\text{C}$  until analysis.

#### Instrumental Analysis

The target compounds in sediment samples were determined by HPLC–tandem mass spectrometry (MS/MS). The instrument system used in the analysis was an Agilent 1200 HPLC system coupled to an Agilent 6460 triple quadrupole mass spectrometer equipped with a precolumn (2.1 mm, 0.2  $\mu\text{m}$ ; Agilent) connected sequentially to a Betasil C18 column (2.1 mm i.d.  $\times$  50 mm length, 5  $\mu\text{m}$ ; Thermo Hypersil-Keystone, Bellefonte, Pennsylvania, USA). The analysis was performed under electrospray negative ionization (ESI) mode with an injection volume of 5  $\mu\text{L}$ . The



mobile phases were 2 mM of ammonium acetate aqueous solution (solvent A) and methanol (solvent B) at a flow rate of 250  $\mu\text{L}/\text{min}$  with the following gradient program: 10 % B at 0 min, increasing to 35 % B at 0.1 min, 55 % B at 7 min, 95 % B at 17 min and kept to 18 min, then back to 10 % B at 20 min. The capillary voltage was held at 3,500 V. The drying and sheath gas flow were set to 6 and 12 L/min, respectively. The drying and sheath gas temperatures were 325 and 350  $^{\circ}\text{C}$ , respectively. Quantification was performed under multiple reaction monitoring (MRM) mode. The instrumental conditions, including MS/MS mass transition, fragmentor, and collision energy, are listed in Table 1.

### Quality Control and Method Performance

Quality-assurance/quality-control procedures were followed during sampling, extraction, and analysis. To decrease instrumental background contamination arising from HPLC or solvents, a ZORBAX SB-Aq trap column (Agilent; 50  $\times$  4.6 mm, 3.5- $\mu\text{m}$  particle size) was inserted in the water-eluent line, immediately above the solvent-mixing cell, as described by Benskin et al. (2007). The LOD and limit of quantification (LOQ) were defined as 3 and 10 times, respectively, of the signal-to-noise (S/N) ratio. The recoveries, method LOD, and method LOQ of each PFAS in sediment are listed in Table S7. The LOQs for the 16 target compounds were 25–100 pg/g, whereas their recoveries ranged from 65.3 to 103.3 %. Blanks (field and procedural) and control samples were run every six samples to check for carryover, background contamination, precision, and accuracy of the recovery. Teflon-coated laboratory ware and glassware were not used to minimize sample contamination from the sampling, pretreatment, and analysis. Glass containers should be avoided for standards, extracts, and samples because PFASs can potentially adsorb onto glassware surfaces.

### Data Analysis

The mass inventory for a chemical in the sediment of a river was calculated by the following equation (Eq. 1):

$$I_s = C_s \times A \times H_s \times \rho, \quad (1)$$

where  $I_s$  is the mass inventory of a chemical in sediment (in kg);  $C_s$  is the median value of a chemical in sediment (in ng/g);  $A$  is the water area [sediment area (in  $\text{km}^2$ )]; and  $H_s$  is the average depth of sediment (in m) with an assumed sediment density ( $\rho$ ) of 1.5  $\text{g}/\text{cm}^3$  and a sediment thickness of 5 cm. For detailed calculation, please refer to a previous study by Chen et al. (2006).

One-way analysis of variance (ANOVA) was used to determine significant differences between concentrations of

PFASs detected in sediments of five rivers (Yellow River, Liao River, Hai River, Zhujiang River, and Dongjiang River) and seasonal variations. Principle component analysis (PCA) was performed to explore the similarity and difference of sampling sites in five rivers. Multiple linear regression analysis was used to determine the relationships between the sediment properties (TOC, texture, and pH) and the concentrations of PFASs. All concentrations of each class of PFAS in sediments of the five rivers during the two seasons (winter and summer) and sediment properties (TOC, texture, and pH) were fitted separately using multiple linear regression. All statistics were performed using SPSS software (version 18.0, SPSS, Chicago, Illinois, USA), and the significance level was set at  $p = 0.05$ .

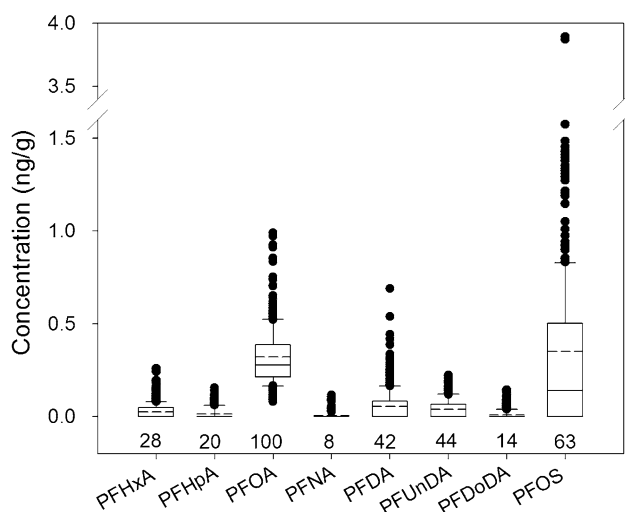
## Results

### Distribution of Perfluoroalkyl Substances in River Sediments

Among the 16 target compounds, 7 PFCAs (PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, and PFDoDA) and 1 PFSA (PFOS) were detected in the sediments of the 5 rivers (Yellow River, Liao River, Hai River, Zhujiang River, and Dongjiang River). Concentration ranges and mean and median values of PFASs in each river are listed in Table S8. The concentration levels of individual compound in sediment in those rivers ranged from <0.008–3.89 ng/g dw. PFOA, PFOS, PFDA, and PFUnDA were the most frequently detected PFASs as shown in Fig. 2. The detection frequencies were 100, 63, 42, and 44 % and the mean concentrations 0.32, 0.35, 0.05, and 0.04 ng/g dw, respectively. Less frequently detected PFASs were PFHpA, PFHxA, PFNA, and PFDoDA with detection frequencies <30 % (Fig. 2). The other PFASs, e.g., PFBA, PFPeA, PFTrDA, PFTeDA, PFBS, PFHxS, and PFDS, were not detected in the sediments of the 5 rivers (Table S8). PFOS and PFOA were dominant PFASs in the sediments of the 5 rivers with median concentrations of 0.14 and 0.28 ng/g dw, respectively. The highest concentration of PFOA (0.99 ng/g dw) was found downstream of Dongjiang River (Fig. 3). The highest level of PFOS detected were 3.89 ng/g dw downstream of Yellow river in Lanzhou city. Total PFASs detected in sediment downstream of the Yellow river in Lanzhou city was also the highest concentration (4.72 ng/g dw) in the 5 rivers.

### Mass Inventory of Perfluoroalkyl Substances in River Sediments

To assess the potential of sediments as a reservoir and secondary source of contamination in the riverine



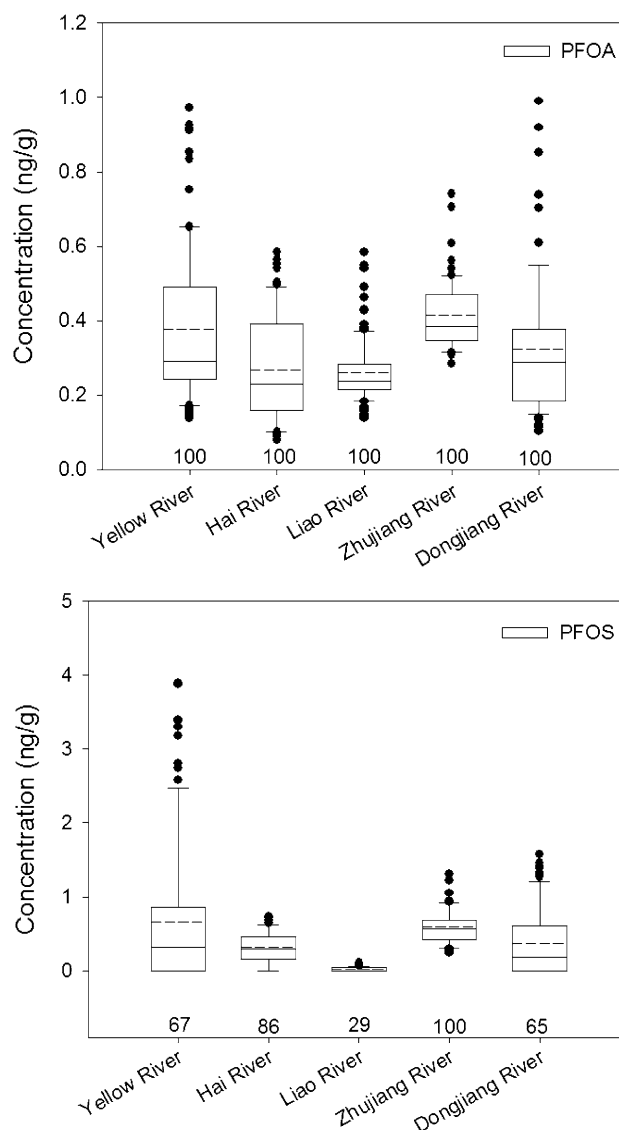
**Fig. 2** Box-plots for perfluoroalkyl substances detected in sediments of the five Chinese rivers (two seasons combined). Each *box-plot* depicts groups of numerical data through their six-number summaries (the smallest, lower quartile, median, mean, upper quartile, and the largest detection). The *dashed line* in the *box* represents mean concentration, and the *solid line* represents median concentration. The number at the *bottom* of each *box* is the detection frequency (%) of corresponding PFASs

environment, mass inventories of PFASs in the river sediments were calculated for the five major Chinese rivers. The mass inventories of PFOA, PFOS, and  $\Sigma$ PFASs are listed in Table 2. The mass inventories of  $\Sigma$ PFASs showed the following order: Dongjiang River (125 kg) > Yellow River (102 kg) > Liao River (31.5 kg) > Zhujiang River (11 kg) > Hai River (8.4 kg). The same trends were found for PFOS and PFOA concentrations in the five river sediments (Table 2) suggesting that this is largely linked to the catchment scales of the five rivers.

#### Relationships Between Chemical Concentrations and Sediment Properties

The relationships between concentrations of PFASs and sediment properties (TOC, texture, and pH) of each river were analyzed by using multiple linear regressions (Table S9). Statistical analysis has shown that sediment organic carbon contents (TOC) were the most consistently correlated with the concentration of PFOS, PFOA, and  $\Sigma$ PFASs in the sediments. There were no significant relationships between PFASs concentration and clay contents in most sediments.

In Zhujiang River, no significant correlations existed between sediment properties and PFOS and PFOA concentrations ( $p > 0.05$ ). However, significant correlations between PFOS and TOC ( $p < 0.05$ ) were found in sediments from Dongjiang River, Hai River, and Yellow River. Sediment organic carbon contents (TOC) were also found



**Fig. 3** Box-plots for PFOA and PFOS detected in sediments of the five Chinese rivers (two seasons combined)

**Table 2** Estimated mass inventories (kg) of PFOA, PFOS, and  $\Sigma$ PFASs in surface sediments of five Chinese rivers

River	$I_{s\text{-PFOA}}^a$	$I_{s\text{-PFOS}}$	$I_{s\text{-}\Sigma\text{PFASs}}$
Yellow River	43.5	48	102
Hai River	2.7	3.4	8.4
Liao River	27	2.3	31.5
Zhujiang River	3.4	5.1	11
Dongjiang River	80.5	50	125

<sup>a</sup>  $I_s$  values were calculated based on the median concentration values for PFOA, PFOS, and  $\Sigma$ PFASs in each river

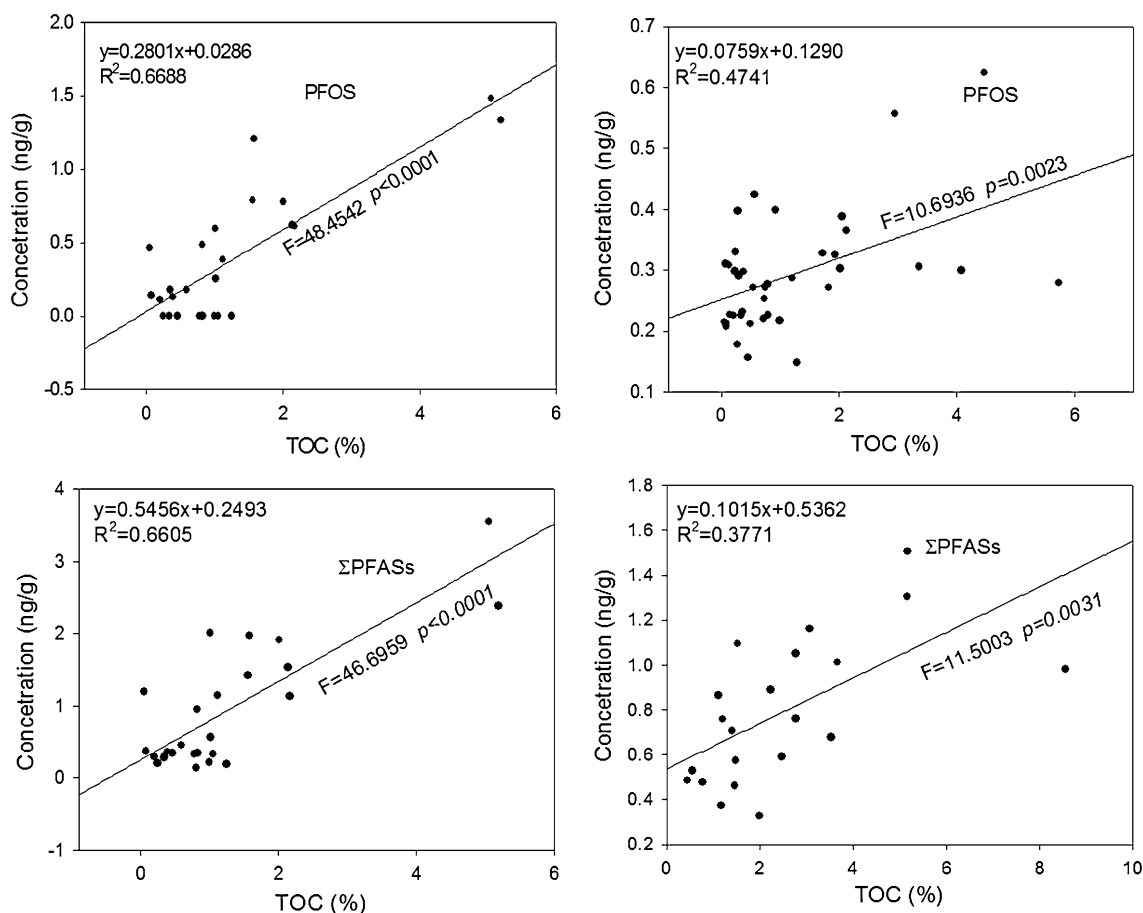
to be significantly correlated to the concentration of  $\Sigma$ PFASs in the sediments of the Dongjiang River and Hai River (Fig. 4).

## Discussion

Among the 16 target PFASs, 8 PFASs (PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFOS) were detected in sediments of the 5 Chinese rivers. In general, no significant seasonal difference was observed for most individual PFASs and  $\Sigma$ PFASs in the 5 rivers except for the Yellow River, where greater concentrations of PFOS and  $\Sigma$ PFASs were found during the wet season than during the dry season ( $p < 0.05$ ) (Table S8). PFOA and PFOS were the two most frequently detected compounds with mean and median values of 0.32 and 0.28 ng/g dw for PFOA and 0.35 and 0.14 ng/g dw for PFOS in the 5 rivers. In comparison, the Yellow River and Zhujiang River showed greater mean and median values for PFOA and PFOS than the other three rivers (Dongjiang River, Hai River, and Liao River) (Table S8).

Some previous studies have determined the PFASs concentrations in sediment globally (Table 3). The concentration levels for the target PFASs in the sediments of the five Chinese rivers were in fact in the same order of magnitude as those reported in the river sediments of other

countries such as Cantabrian River (Gomez et al. 2011), Ganges River (Corsolini et al. 2012), Parramatta River (Thompson et al. 2011), Orge River (Labadie and Chevreuil 2011), and San Francisco River (Higgins et al. 2005) (Table 3). However, mean concentrations for PFOA in the five Chinese rivers were much lower than those in the Ganges River in India (8.57 ng/g dw) (Corsolini et al. 2012) and the Tenjin River in Japan (2.1 ng/g dw) (Senthilkumar et al. 2007), whereas mean concentrations for PFOS in the five Chinese rivers were much lower than in Tenjin River and Katsura River of Japan (11 and 2.3 ng/g dw, respectively) (Senthilkumar et al. 2007), Orge River of France (4.3 ng/g dw) (Labadie and Chevreuil 2011) and Parramatta River of Australia (2.1 ng/g dw) (Thompson et al. 2011). Mean concentrations for PFOA and PFOS in the five Chinese rivers were much greater than that of five rivers and lakes in Korea (0.05 and 0.12 ng/g dw for PFOA and PFOS, respectively) (Lam et al. 2014). The difference of the PFASs concentrations among different rivers may be caused by the pollution source, wastewater-treatment method, discharge volume, number and location of the sampling sites, river characteristics, chemical



**Fig. 4** Correlations between TOC and chemical concentrations of PFOS and  $\Sigma$ PFASs in sediments of Dongjiang River and Hai River

**Table 3** Comparisons of concentrations ranges (median or mean) of perfluoroalkyl substances in the sediments from five major Chinese rivers and those from other rivers in the world

Compound	Asia					America			Europe		Australia
	China					Japan	Korea	USA	Spain	France	Australia
	Yellow River	Hai River	Liao River	Zhujiang River	Dongjiang River	Tenjin River	Rivers and lakes	San Francisco River	Cantabrian River	Orge River <sup>b</sup>	Parramatta River <sup>b</sup>
PFHxA	<LOD-0.19 (<LOD)	<LOD-0.05 (<LOD)	<LOD	<LOD-0.15 (0.06)	<LOD-0.25 (<LOD)		<LOD-0.05 (0.01)	<LOD-0.05 (0.229)		0.05-0.07 (0.06)	<LOD
PFHpA	<LOD-0.09 (<LOD) <sup>a</sup>	<LOD	<LOD	<LOD-0.11 (0.05)	<LOD-0.15 (<LOD)		<LOD-0.06 (<LOD)	<LOD-0.06 (0.194)		0.02-0.04 (0.03)	<LOQ
PFOA	0.14-0.93 (0.29)	0.09-0.53 (0.23)	0.15-0.42 (0.24)	0.31-0.68 (0.38)	0.13-0.92 (0.29)	2.1	<LOD-0.28 (0.05)	<LOD-0.39 (0.229)	<LOD-0.02 (<LOD)	<LOD	<LOD-0.16 (0.03)
PFNA	<LOD-0.11 (<LOD)	<LOD	<LOD-0.03 (<LOD)	<LOD	<LOD		<LOD-0.15 (0.04)	<LOD-0.237 (<LOD)	<LOD	0.04-0.06 (0.05)	<0.10-0.11 (0.04)
PFDA	<LOD	0.05-0.29 (0.09)	<LOD-0.04 (<LOD)	0.04-0.41 (0.11)	<LOD-0.42 (0.02)		<LOD-0.08 (0.03)	<LOD-1.11 (0.194)		0.01-0.05 (0.03)	<LOD-0.81 (0.26)
PFUnDA	<LOD-0.16 (<LOD)	<LOD-0.14 (0.05)	<LOD-0.05 (<LOD)	<LOD-0.19 (0.09)	<LOD-0.20 (0.05)		<LOD-0.09 (0.04)	<LOD-0.396 (<LOD)		0.28-0.30 (0.29)	0.1-0.61 (0.22)
PFDoDA	<LOD	<LOD-0.11 (<LOD)	<LOD	<LOD-0.06 (<LOD)	<LOD-0.14 (<LOD)	2.4	0.01-0.13 (0.05)	<LOD-0.584 (<LOD)		1.7 (1.7)	<LOD-1.1 (0.34)
PFTtDA	<LOD	<LOD	<LOD	<LOD	<LOD			<LOD-0.435 (<LOD)		0.29-0.31 (0.30)	<0.1-0.27 (0.07)
PFTEdA	<LOD	<LOD	<LOD	<LOD	<LOD					0.83-0.89 (0.86)	<LOD
PFBS	<LOD	<LOD	<LOD	<LOD	<LOD	<1.0			<LOD	<LOD	<LOD
PFHxS	<LOD	<LOD	<LOD	<LOD	<LOD	<1.4	<LOD-0.01 (0.00)	<LOD	<LOD	0.08-0.12 (0.10)	<0.1-0.1 (0.04)
PFOS	<LOD-3.69 (0.32)	<LOD-0.71 (0.30)	<LOD-0.10 (<LOD)	0.27-1.28 (0.57)	<LOD-1.48 (0.18)	11	0.01-0.48 (0.12)	<LOD-3.76 (0.288)	<LOD-0.13 (0.03)	4.0-4.6 (4.3)	0.8-6.2 (2.1)
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD		<LOD			0.11-0.13 (0.12)	<0.1-0.20 (0.06)
Reference	This study	This study	This study	This study	This study			Higgins et al. 2005	Gomez et al. 2011.	Labadie and Chevretuil 2011	Thompson et al. 2011

LOD Limit of detection, LOQ limit of quantitation

<sup>a</sup> Values in parentheses are median values

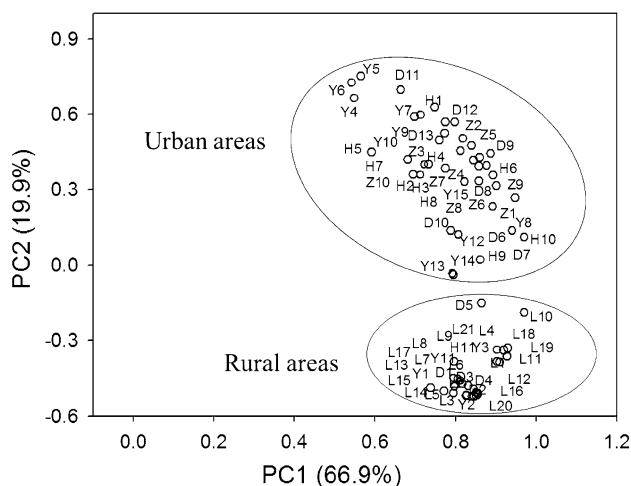
<sup>b</sup> Values in parentheses of this column are mean values



solubility, etc. Lower PFAS concentrations levels were observed in these five rivers because the sites selected for the present study are located in the main streams, and greater concentration levels are usually expected to be found in the tributaries, which often receive discharge of wastewaters.

Three previous papers reported PFAS concentrations in sediment of Hai River, Liao River, and the Guangzhou section of Zhujiang River, from which sediments were sampled in 2008, 2009, and 2010, respectively (Bao et al. 2009, 2010; Li et al. 2011a). Compared with previous data, PFAS concentrations in sediment of the Guangzhou section of Zhujiang River and Liao River in this study were almost at the same level with the corresponding river reported previously. This could be caused by the sampling time periods being almost the same as in these two rivers and there being no obvious difference of PFAS input to these two rivers. However, PFAS concentrations in Hai River ( $\Sigma$ PFASs = 0.48–1.51 ng/g dw) in this study were much lower than those of the sediments sampled in 2010 ( $\Sigma$ PFASs = 07.1–16 ng/g dw) suggesting the increasing of PFAS and discharge alone in Hai River during the year 2009–2010. Tianjin Binhai, the new area, should be responsible for the sharp increase in PFAS concentrations.

PCA showed source-related spatial variations for PFASs in the five Chinese rivers with sampling sites being approximately separated into two groups (urban vs. rural areas) (Fig. 5). The sites located in the urban areas shown relatively greater concentration levels of PFASs (0.33–4.72 ng/g dw), whereas those sites located in the rural areas had lower concentration levels (0.10–0.60 ng/g dw). Sites (Y4 to Y6, Z1 to Z10, and D8 to D13) located in the industrial cities of Lanzhou, Guangzhou, and Dongguan, respectively, received discharge of domestic and industrial wastewaters, which



**Fig. 5** PC loading for sampling sites in five Chinese rivers based on the compositions and concentrations of PFASs in the river sediments

often contain various PFASs with mean PFOS concentrations of 264.7 ng/L in municipal wastewater-treatment plant (WWTP) effluents and 5663.3 ng/L in industrial WWTP effluents (Lin et al. 2010).

In addition to pollution sources, spatial variations for PFASs in river sediments could also be influenced by other factors such as river flow, suspended particles, and sediment properties. As listed in Table 2, Dongjiang River, Zhujiang River, and Yellow River had much greater water flows than Hai River and Liao River. High flows can dilute the chemical concentrations in water phase, but they also bring more chemicals into the riverine environments, thus resulting relatively greater chemical levels in river sediments. Moreover, Yellow River has high levels of suspended particles (Yang et al. 2000), which could increase the sorption of chemicals onto solid phase. The distribution of PFASs in sediment depends on various factors such as pollution degree, sediment properties, and physicochemical properties of the chemical (such as chain length). Sorption process of a chemical plays an important role in the distribution of PFASs (Higgins and Luthy 2006; Ahrens et al. 2009). Sediment TOC and texture were found to be the most important sediment properties that positively correlated with PFASs compounds, which is consistent with previous studies (Higgins and Luthy 2006; Ahrens et al. 2009; Labadie and Chevreuil 2011). High sorption is often associated with high TOC in sediment. The pH was also correlated with PFASs in sediments; this is probably due to its effects on cation bridging, cation exchange, and electrostatic interactions between a chemical and sediment phase. Higgins and Luthy (2006) also found that adsorption of PFASs on sediments also increased with increasing metal cations and decreasing pH value. The results of the present study showed that the concentration levels of some PFASs in some rivers significantly correlated to sediment organic carbon contents but not with other properties such as clay contents and pH values.

Results of the present and previous studies showed that river sediments are an important reservoir of PFASs in the riverine environment. However, river sediments can also be a secondary source for PFASs in the riverine environment because these PFASs can undergo desorption process and release back to the water phase (You et al. 2010). In fact Martin et al. (2004) suggested that sediments are the major source of PFASs into the biota food web. Therefore, PFASs in river sediments could pose potential risks to aquatic organisms and furthermore to humans. However, the maximum concentration (3.89 ng/g dw) for PFOS found in the present study is lower than the predicted no-effect concentration of 67 ng/g (Brooke et al. 2004) suggesting that ecological risk of sediment PFASs in these Chinese rivers is not likely to happen. However, long carbon-chain PFASs are persistent and bioaccumulative with bioconcentration

factors for PFOS in lake trout, turtle, and spotted sea trout of 34000, 11000, and 9800, respectively (Houde et al. 2006, 2008; Morikawa et al. 2006). Quinete et al. (2009) reported that the biomagnification factors for PFOS in tucuxi dolphin ranged from 7.7 to 63, thus indicating that PFOS has strong bioconcentration and biomagnification ability. Moreover, PFOS has been proved to cause various adverse biological effects (such as negative effect on enterohepatic circulation and cholesterol metabolism) (Kudo and Kawashima 2003; Fletcher et al. 2013). However, regulatory efforts have been made to decrease the production of certain PFASs (PFOS and related POSF), and temporal studies have already showed an environmental response to changes in production and use (Chengelis et al. 2009; Zhang et al. 2013). Given this, the adverse effects of PFOS would be less and less in riverine environment in the long term. But long-term risks to aquatic organisms or even human from PFASs, such as PFOS, should not be neglected.

## Conclusions

The results from this study provided national baseline data for PFASs in the sediments of major Chinese rivers. PFASs, especially PFOA and PFOS, were found to be prevalent in the five major Chinese rivers (Yellow River, Hai River, Liao River, Zhujiang River, and Dongjiang River) at concentrations ranging from not detected to 3.89 ng/g dw. PFOA was detected with the highest frequency, and PFOS was detected with the highest concentration (3.89 ng/g dw in Yellow River sediment) among the five rivers. High PFAS concentration levels were often found to be associated with sites in urban areas, thus suggesting the significant contribution from domestic and industrial wastewater discharges. The distribution of PFASs in the river sediments was also influenced by sediment properties, such as sediment organic content, suggesting the important role of partitioning process in the distribution of PFASs in the riverine environment. Further studies should develop the ultra-high sensitivity and simultaneous method for PFASs precursors and branched-chain isomers in different matrix. Column sampling and sediment dating ( $^{137}\text{Cs}$  and  $^{210}\text{Pb}$ ) are also needed in future studies. Meanwhile, it is also essential to include sampling sites in small tributaries and point sources for source identification, thus facilitating adopting proper measures to control and prevent pollution of PFASs.

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