



Perfluoroalkyl acids in surface waters and tapwater in the Qiantang River watershed—Influences from paper, textile, and leather industries



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HIGHLIGHTS

- PFASs in waters in textile, leather, and paper making industrial areas were analyzed.
- The Qiantang River was among the most PFAS-contaminated rivers in China.
- PFASs in surface water and tapwater samples were compared.
- There are correlations between PFAS isomer profiles in tapwater and surface waters.

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ABSTRACT

Perfluoroalkyl acids (PFAAs) are widely used as multi-purpose surfactants or water/oil repellents. In order to understand the contamination level and compositional profiles of PFAAs in aqueous environment in textile, leather, and paper making industrial areas, surface waters and tap waters were collected along the watershed of the Qiantang River where China's largest textile, leather, and paper making industrial bases are located. For comparison, surface water and tapwater samples were also collected in Hangzhou and its adjacent areas. 17 PFAAs were analyzed by solid phase extraction-high performance liquid chromatography-tandem mass spectrometry. The results show that the total concentrations of PFAAs (Σ PFAAs) in the Qiantang River waters ranged from 106.1 to 322.9 ng/L, averaging 164.2 ng/L. The contamination levels have been found to be extremely high, comparable to the levels of the most serious PFAA contamination in surface waters of China. The PFAA composition profiles were characterized by the dominant PFOA (average 58.1% of the total PFAAs), and PFHxA (average 18.8%). The Σ PFAAs in tap water ranged from 9.5 to 174.8 ng/L, showing PFAA compositional pattern similar to the surface waters. Good correlations between PFAA composition profiles in tap waters and the surface waters were observed.

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1. Introduction

Perfluoroalkyl acids (PFAAs) are organofluorine compounds containing only carbon-fluorine bonds (no C–H bonds) and C–C bonds but also function groups such as carboxyl and sulfonic acid groups. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic

acid (PFOS) are the most investigated PFAAs, which have been widely produced and frequently detected in the environment (Yamazaki et al., 2016). Toxicity studies on PFAAs and ecological risk assessment have shown that certain PFAAs have acute and chronic toxicity and may accumulate in the food chain and concentrate in the human body, posing a potential threat to human health (Olsen et al., 2009; Stahl et al., 2011; USEPA, 2009, 2016). Due to their high stability and excellent hydrophobic and oleophobic properties, PFAAs are widely used as the multi-purpose surfactants in textile (Berger and Herzke, 2006), leather (Kotthoff et al., 2015), paper

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industries, and other fields (Prevedouros et al., 2006). The wide use of perfluoroalkyl substances as scouring and waterproofing agents in paper, textile and leather product industries has been recognized. For example, it has been reported that leather furniture and shoes contain PFOS of 38 $\mu\text{g}/\text{m}^2$ and 21 $\mu\text{g}/\text{m}^2$ respectively and PFBA, PFHxA, 8:2 FTOH, and 10:2 FTOH have been found in leather shoes (Fiedler et al., 2010; Müller and Schlummer, 2011; Herzke et al., 2012; Vestergren et al., 2015).

Widespread contamination of PFAAs in China's aqueous environments such as the mid- and low-reaches of the Yangtze River has been reported (Lu et al., 2011, 2015). However, due to the diversification of sources of PFAAs (sewage, industrial effluents, atmospheric precipitation, solid waste landfill leaching, etc.), the source identification of PFAAs in surface water is complicated in the Yangtze River Delta region. In order to identify the sources of PFAAs in environmental surface waters and their impact on tapwater in particular industrial areas, such as paper, textile, and leather industrial areas, the mid- and lower reaches of the Qiantang River (the upper stretch is called the Fuchun River) in East China and its watershed are chosen as the investigated area in this paper.

As an important commercial artery, the Qiantang River runs for 459 km through Zhejiang Province, passing through the provincial capital Hangzhou before flowing into the East China Sea via Hangzhou Bay. Many industries are located along the river. For example, Hangzhou is a “Town of Paper Making” in China, and Xiaoshan, a textile industrial base area, and Hai'ning, “the capital of leather industry of China”. High PFOA concentration in samples of wastewater discharged from textile manufacturing facilities in Xiaoshan (Greenpeace, 2011a, 2011b; Brigden et al., 2012) has been reported. However, the detailed information on the composition profiles of PFAAs in the textile, paper, and leather industrial areas were still unknown. In this paper, 17 PFAA compounds in surface waters of the Qiantang River watershed were analyzed, and for comparison, surface water and tapwater samples were also collected in Hangzhou and its adjacent areas in East China. The features of PFAA isomer compositions in each area are discussed for better understanding of the sources and the impact of PFAAs in surface waters on the tap waters in these specific industrial areas.

2. Material and methods

2.1. Sample collection

A total of 69 surface water samples and 14 tap water samples were collected in the Qiantang River watershed and the adjacent cities in April and June in 2015 (Fig. 1). Tap water samples were collected directly using 1-L polypropylene (PP) bottles. Surface water samples were collected with a stainless steel bucket and then transferred into PP bottles. All samples were collected from the upper 1 m depth. Two parallel surface water samples of 500 mL in the urban areas, and at least 1 L surface water samples in the rural areas were taken at each sampling site to ensure that the detection limit of the analytical method used was met. All samples were stored in PP bottles at 4 °C until analysis (Taniyasu et al., 2005; Lu et al., 2011). The field blank and travel blank samples were Millipore water. Detailed information about each sampling site is summarized in Supplementary Information Table S1.

2.2. Reagents

Potassium salts of perfluorooctane sulphonate (PFOS), perfluorohexane sulfonate (PFHxS), perfluorobutane sulfonate (PFBS), perfluorodecane sulfonate (PFDS), perfluorobutanoic acid (PFBA), perfluorononanoic acid (PFNA), perfluorooctanoic acid (PFOA), perfluoroheptanoic acid (PFHpA), perfluoropentanoic acid (PFPeA),

and perfluorohexanoic acid (PFHxA) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Perfluorododecanoic acid (PFDoDA), perfluoroundecanoic acid (PFUnDA), perfluorodecanoic acid (PFDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA), and perfluorotetradecanoic acid (PFTrDA) were purchased from Fluorochem Ltd. (Derbyshire, UK). $^{13}\text{C}_4$ -PFOS, $^{13}\text{C}_2$ -PFDA, $^{13}\text{C}_5$ -PFNA, $^{13}\text{C}_4$ -PFOA, $^{13}\text{C}_4$ -PFBA, $^{13}\text{C}_2$ PFHxA, $^{13}\text{C}_2$ PFUnDA, $^{13}\text{C}_2$ PFDoDA, and $^{18}\text{O}_2$ PFHxS were purchased from Wellington Laboratories Inc. (ON, Canada). The chemical purity of all the standards was >95%.

Oasis weak anion exchange (WAX; 6 cm^2 , 150 mg, 30 mm) solid phase extraction (SPE) cartridges were purchased from Waters Corp. (Milford, MA, USA). Milli-Q water was used during the course of the experiment. Methanol (residual pesticide and PCB analytical grade), ammonium acetate (97%), ammonium solution (25%), and acetic acid (99.9%) were obtained from Wako Pure Chemical Industries Ltd.

2.3. Pretreatment and purification

Water samples were analyzed for 17 PFAAs, including PFOS, PFHxS, PFBS, PFDS, PFODA, PFHxA, PFTeDA, PFDoDA, PFUnDA, PFDA, PFOA, PFNA, PFBA, PFHpA, PFPeA, PFHxDA, and PFTrDA. Full method details including quality control and quality assurance procedures were as described in previous reports (Lu et al., 2011) based on ISO25101 (ISO25101, 2009; Taniyasu et al., 2013). Briefly, the cartridge was pre-conditioned by passing through a sequence of 4 mL of 0.1% ammonia/methanol, 4 mL of methanol, and 4 mL of Milli-Q water. The unfiltered water samples (250 mL) were spiked with mass-labeled standards and passed through the wet Oasis® WAX cartridge at the rate of 1–2 drop/s (Taniyasu et al., 2005, 2013). After loading all samples, cartridges were rinsed with 4 mL of 25 mM acetate buffer solution (pH 4) and this portion was discarded. The water remaining in the cartridge was completely removed by centrifugation at 3000 rpm for 20 min at room temperature. The target analytes were eluted with 4 mL of methanol followed by 4 mL of 0.1% NH_4OH . The effluent was concentrated to 1 mL under a stream of high purity nitrogen.

2.4. Instrumental quantification

PFAAs were determined using a tandem mass spectrometer (API 4000, Applied Biosystems Inc., Framingham, MA, USA) coupled with a high performance liquid chromatography (HPLC) (Agilent Technologies 1200) operated in the electrospray negative ion mode. The LC column used was an RSpak JJ-50 2D ion exchange column (2.0 mm \times 150 mm, 5 μm ; Shodex, China). The injection volume was 10 μL . The analytes were eluted with 50 mmol/L ammonium acetate–methanol mixed solution (volume ratio 2:8) in isocratic elution mode at a flow rate of 300 $\mu\text{L}\text{min}^{-1}$ for 20 min. The column temperature was 40 °C. The electrospray ionization voltage was 4000 V, using negative mode ion source, and the ion source temperature was 350 °C. The curtain gas pressure was 69 KPa, the ion source GAS1 pressure was 344.7 KPa, the ion source GAS2 pressure was 344.7 KPa and the collision gas pressure was 34.5 KPa. Multiple reaction monitoring (MRM) mode was used. Calibration curves for the instrument were prepared with a series of seven concentrations at 0, 2, 10, 50, 200, 1000, 5000, and 25000 pg/mL . The instrumental response of target analytes was confirmed for quantification using individual chromatograms.

2.5. Quality assurance and quality control (QA/QC)

To achieve lower detection limits, all of the accessible PTFE and



Fig. 1. Map of the research area and the sampling sites along the Fuchun and Qiantang Rivers.

fluoropolymer materials in the HPLC instrument and apparatus were replaced with materials made of polyetheretherketones (PEEK) to minimize any background signal caused by contamination (Yamashita et al., 2005). Procedure and travel blanks for water were collected. The recovery test was carried out using both surrogates and native standard chemicals. If the recovery exceeded the acceptable range (65–125%), samples were reanalysed. Matrix recoveries were also conducted by adding surrogates and native standard chemicals to real samples. Quantitative responses according to the amount of standards added were evaluated. Concentrations of analytes were calculated using an external calibration curve.

The accuracy evaluation was performed by recovery and intermediate precision tests with real environmental water samples, tapwater samples and Milli-Q water. Blanks and recoveries were extracted in duplicate for every 12 samples to ensure stable repeatability. Table S2 presents recoveries and the method quantification limits for individual PFAAs in water samples analyzed in this study. Repeatability of recovery of the present method was tested and the results are shown in Table S3. For matrix-spiked water samples, only the repeatability of recovery of PFHxDA and PFOcDA showed high variability. For calculations of mean concentrations and standard deviation (SD), individual congener concentrations below the MQLs were assigned a value equal to the MQLs divided by the square root of 2.

3. Results and discussion

3.1. PFAAs in surface waters along the Qiantang River

10 PFAAs were quantified in surface waters of the Qiantang River. Detailed concentrations of individual PFAA compounds are provided in Supplementary Table S1. Fig. 2 shows the geographical distribution of the total PFAA concentration (Σ PFAAs) in waters along the Qiantang River. The Σ PFAAs ranged from 108.3 ng/L at Tonglu (sampling site 3) to 322.9 ng/L at Dingqiao of Hai'ning

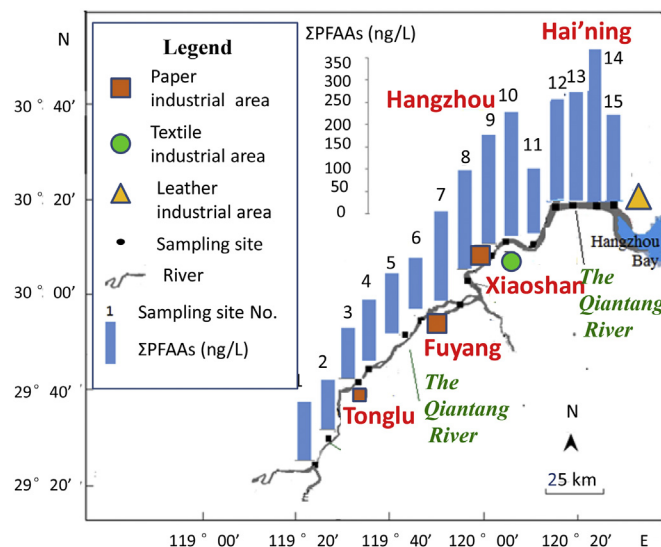


Fig. 2. Geographical distribution of Σ PFAAs in surface waters along the Qiantang River and its upstream (the Fuchun River).

County (site 14) with the mean of 163.6 ± 59.9 ng/L. Of the 17 analytes, PFOA, PFNA, PFBA, PFPea, PFHxA, PFHpA, PFOS, PFBS, PFDA, and PFHxS were detected in most of the samples. PFDS and long-chain PFCAs (C10–C18) PFDA, PFUnDA, PFDODA, PFTrDA, PFTeDA, PFHxDA, PFOcDA, and PFTrDA were not detected or at very low detection rates.

Two significant increases in Σ PFAAs were observed: Σ PFAAs increased by a factor of 2 from sampling site 7 to site 10 in Fuyang; with a maximum concentration of 221.9 ng/L and increased from site 12 to 14 in Hai'ning area; with a maximum concentration of 322.9 ng/L respectively. The composition profiles also changed along the Qiantang River. In the section of Tonglu, PFHxA was the predominant compound followed by PFOA (Fig. 3), whereas in the

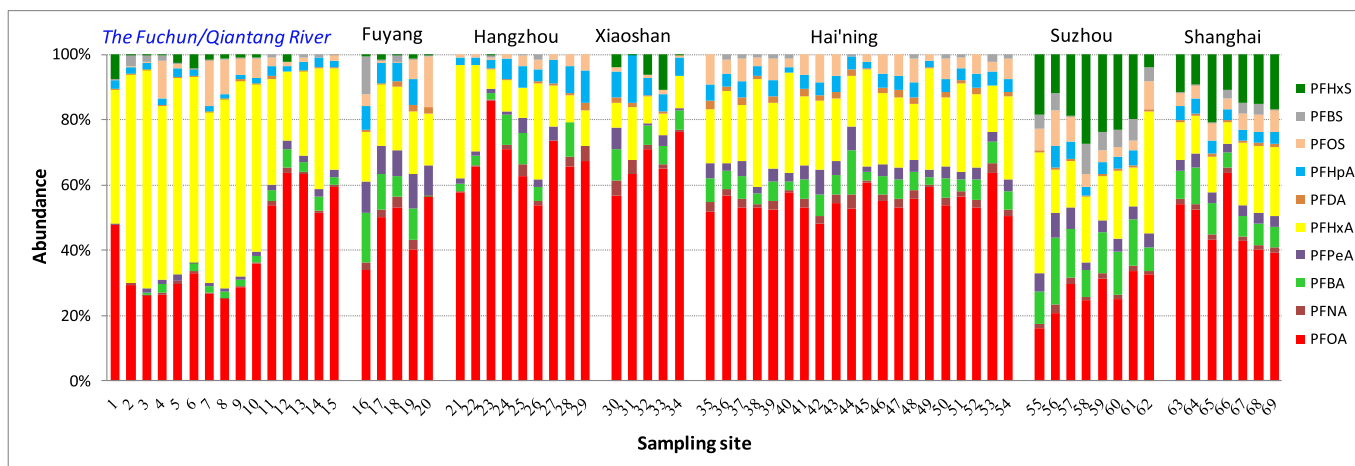


Fig. 3. The relative abundance of each PFAS compound in river waters along the Qiantang/Fuchun River and surface waters from Hai'ning, Xiaoshan, Hangzhou, Suzhou, and Shanghai.

Hangzhou section, PFOA increased while PFHxA began to decrease. In the Hai'ning section of the Qiantang River, PFOA was the dominant (59.4%) compound followed by PFHxA (28.9%). The possible sources are likely the paper, textile, and leather industries along the Qiantang River. The C6 compound PFHxA is widely used in waterproofing agent for these industries (Kärman et al., 2006).

Wang et al. (2016) investigate the mass discharges of PFAAs and some fluorinated alternatives from the Qiantang River. They observed high levels of PFOA (average 211 ng/L, 83% of total PFAAs) in Qiantang River together with elevated levels of PFHxA (average 26.8 ng/L) which is in consistency with the results of higher PFOA in the Hai'ning section of the Qiantang River in our study. Compared with reported Σ PFAAs in surface waters in Eastern China, the highest Σ PFAAs observed in this study are comparable to those in Shanghai (170 ng/L, Lu et al., 2015; 352 ng/L, Wang et al., 2016) and higher than those of the Grand Canal of China (7.8–218.0 ng/L, Chen et al., 2016), and Taihu Lake water (164–299 ng/L; Pan et al., 2014). The Σ PFAS concentrations observed in this study are higher than the levels in some rivers and lakes in the World such as the Elbe River (26.4 ng/L; Ahrens et al., 2009), the Po River, Italy (146 ng/L, Valsecchi et al., 2014), the Great Lakes of U.S. (PFOA: 21–70 ng/L, Boulanger et al., 2004), and Lake Biwa in Japan (PFOA: 7.0–26 ng/L, Tsuda et al., 2010).

The PFAA composition profiles in the textile industrial area (Xiaoshan) similar to the leather industrial area (Hai'ning) were observed. These composition profiles showed significant difference from those in the adjacent areas such as Suzhou and Shanghai where higher PFHxS was observed (Fig. 3). Suzhou and Shanghai are both densely populated metropolitan cities with various types of industries; therefore the composition profiles in Suzhou and Shanghai may reflect multiple industrial pollution sources as well as effluents of municipal waste water treatment plants (WWTPs). Hence, the increase of PFHxS in surface waters from Suzhou and Shanghai was likely caused by different types of pollution sources from the Qiantang River watershed areas. The characteristics of contamination levels and composition profiles in each specific industrial area will be discussed in detail in the following sections.

3.2. The paper industrial areas

The paper manufacturers in the studied areas are mainly distributed in Fuyang and Yuhang District of Hangzhou City. Fuyang District in the mid-reach of the Qiantang River is the famous “Town

of Paper Making” in China, with 1000-year paper-making history and more than 300 paper mills, accounting for one third of paper production in Zhejiang Province. Further upstream in Tonglu, there are the industries with product mainly as tail paper, CAD drawing paper, and film coated base paper for food packaging.

The total concentrations and composition profiles of PFAAs in surface water samples of the paper industrial areas including West Lake and river water samples in the Grand Canal in Hangzhou City and Jiaxing County are shown in Fig. 4(a). The Σ PFAAs in surface water of Fuyang and Hangzhou City were in the range from 94.3 to 179.3 ng/L, with the mean of 122.3 ± 32.1 ng/L. Different from waters in the upper reach of the Qiantang River (site 1–10), the Hangzhou City surface water was characterized by high proportion of PFOA, averagely accounting for 65.8% of the total PFAAs, followed by PFHxA (16.1%) and PFBA (3%). Separated by the Qiantang River, the compositions of PFAAs in surface waters in Hangzhou City downtown area were similar to those of Hai'ning area in the north bank of the river rather than Xiaoshan area in the south bank, suggesting that the Hangzhou City downtown area and Hai'ning may share the same type of sources of PFAAs.

The composition profile of PFAAs in the Grand Canal waters of the Hangzhou section was different from the rest of the Grand Canal sections in China (Piao et al., 2017). The Σ PFAAs in the Grand Canal water gradually decreased from the intersection of the Grand Canal and the Qiantang River (also the starting point of the Grand Canal) to Jiaxing County (Fig. 4(a)). The PFAA composition profile was slightly different in the Jiaxing section from that in the Hangzhou section, with the increasing of PFOS and PFHpA (site 27–29), but keeping the main feature of the composition profile of Hangzhou.

3.3. The textile industrial areas

There are totally 500 textile enterprises in Xiaoshan covering a complete industrial chain including chemical fibers, cotton spinning, dyeing and printing. The geographical distribution of the mean total concentrations of PFAAs in surface waters from Xiaoshan District of Hangzhou is shown in Fig. 4(a). Compared with the Hangzhou City and Hai'ning surface waters, the Σ PFAAs in surface water of Xiaoshan area were generally at a higher level, in the range from 87.6 to 202.7 ng/L averaging 167.3 ± 45.7 ng/L. The higher Σ PFAAs were observed at sampling sites where several textile industries with application of dyeing and finishing

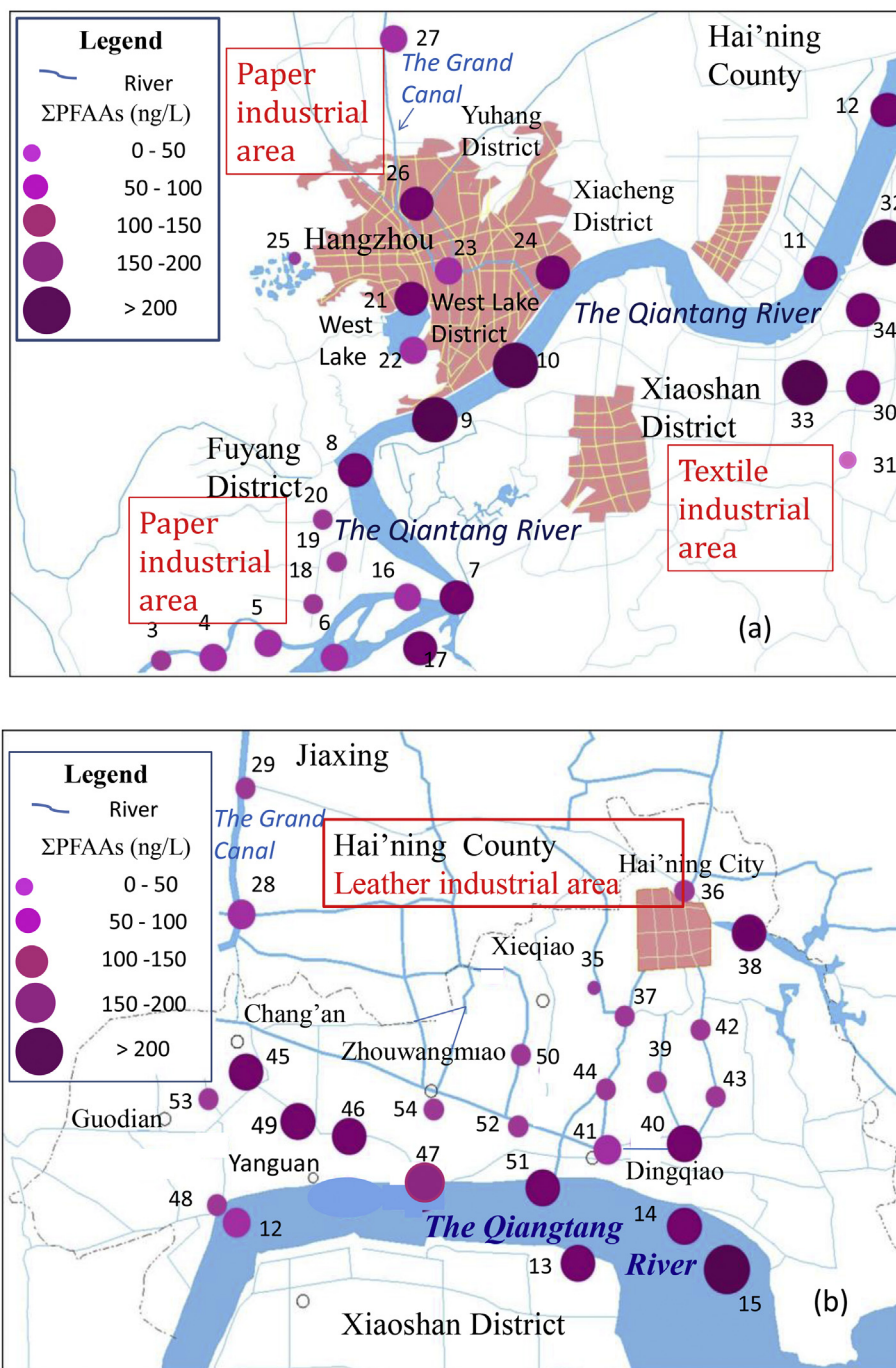


Fig. 4. Map of the sampling sites and the geographical distribution of Σ PFASs in (a) Fuyang, Hangzhou, and Xiaoshan areas, and (b) Hai'ning area.

auxiliaries were located nearby. The Σ PFASs in surface water of Xiaoshan area were comparable to the most polluted areas such as the Yangtze River Delta area (42.4–170 ng/L), Shenyang (17–240 ng/L) (Lu et al., 2011), and Shanghai (39–212 ng/L, Lu et al., 2015). The Qiantang River water sample (site 33) from the Xiaoshan side showed high Σ PFASs (245.9 ng/L), suggesting that industrial wastewaters involved in the manufacture of textiles may have been directly discharged into the Qiantang River (Brigden et al., 2012).

The PFASs were dominated by PFOA, averagely accounting for 65.8% of the total PFASs, followed by PFHxA (11.5%) and PFBA (5.6%). The concentrations of PFOA (averaging 119.6 ng/L) in Xiaoshan surface water samples are consistent with the reported

PFOA concentrations in samples of wastewater discharged from textile manufacturing facilities (Greenpeace, 2011a, 2011b; Brigden et al., 2012). The composition of PFASs in the surface waters of Xiaoshan area were generally in a similar pattern to that observed in the Hai'ning area, but the obvious difference of PFHxS in Xiaoshan and Hai'ning areas were the occurrence of PFHxS in Xiaoshan while PFHxS was nearly undetected in Hai'ning. The PFHxS proportion in Xiaoshan surface waters was up to 11.0%. Our results suggest that there is no much difference between the compositions of PFASs in leather and textile industrial areas except for the occurrence of PFHxS and the significant higher contamination level in the Xiaoshan surface waters.

3.4. The leather industrial area

The geographical distribution of the total concentrations of PFAAs in surface waters from seven towns of Hai'ning County (Chang'an, Dingqiao, Yan'guan, Xieqiao, Zhouwangmiao, Guodian, and Hai'ning City proper) is shown in Fig. 4(b). Detailed concentrations of individual PFAA compounds are provided in [Supplementary Table S1](#).

Of the 17 analytes, PFOA, PFNA, PFBA, PFPeA, PFHxA, PFHpA, PFOS, PFBS, PFDA, and PFHxS were detected in most of the samples. PFDS, PFPrS, and long-chain PFCAs (C10–C18) PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, PFOcDA, and PFTTrDA were not detected or at very low detection rates. The Σ PFAAs in surface water of Hai'ning area were in the range of 57.6–186.7 ng/L, with the mean of 95.9 ± 34.0 ng/L. There are more than 200 leather-related enterprises in Hai'ning County, but the large leather factories are located in Chang'an, Dingqiao, and Guodian. Higher Σ PFAAs were observed at sampling sites at Dingqiao (186.7 ng/L), Chang'an (179.5 ng/L), and Guodian (131.2 ng/L). The lowest Σ PFAAs (57.6 ng/L) were observed in Hai'ning City proper. The five Qiantang River water samples from the Hai'ning side section showed high Σ PFAAs ranging from 129.4 to 322.9 ng/L, averaging 200.1 ng/L.

The composition profiles of PFAAs in each surface water sample of Hai'ning area were generally in a similar pattern characterized by high proportions of PFOA which accounted for 58.3% of the total PFAAs on average, followed by PFHxA (23.1%) and PFBA (5.5%). The PFOA proportions in surface waters of Hai'ning area were significantly higher than those of the adjacent regions such as Suzhou (20.7%) and Taihu Lake (26.0%). PFHxS was nearly undetected in Hai'ning, in contrast to Xiaoshan. The Qiantang River water collected from the Hai'ning side also showed a similar pattern, with PFOA accounting for 61.1% of the total PFAAs on average.

3.5. Influence on tap waters

Detailed concentrations of individual PFAA compounds in the tapwater samples are provided in [Supplementary Table S1](#) (the sample No.: 70–83). The total concentrations of perfluoroalkyl acids in six tap water samples from Hai'ning and Hangzhou ranged from 9.5 to 175.3 ng/L. On the basis of the US EPA reference values of healthy drinking water that PFOA and PFOS at individual or combined concentrations should be less than 70 parts per trillion, (USEPA, 2016), PFAAs in the current Hangzhou and Hai'ning tap waters have not posed a health risk to the local residents. Compared with the other cities in China, PFAAs in tap water from

Hai'ning and Hangzhou were at a level from moderate to high pollution, higher than those of Tokyo, Japan, Thailand, and Vietnam, but lower than that reported for France and the United States (Table 1).

PFOA accounted for 61.1% of the Σ PFAAs in the tap waters of Hangzhou and Hai'ning, followed by PFHxA (17%) and PFBA (6%). Compared with the early reports on PFOS and PFOA in tap water in China (Jin et al., 2009; Mak et al., 2009), the proportion of PFOS in tap water samples of the current study was lower (averagely 6.4%), suggesting an effect of ban of production and usage of PFOS in China in recent years. The composition of PFAAs in the tap waters in Hangzhou and Hai'ning was more close to those of the surface waters in Hangzhou and Hai'ning areas and also the Qiantang River water but significantly different from those of tap waters in the adjacent cities such as Suzhou and Shanghai (Fig. 5). The source of tap waters in Hangzhou is mainly the Qiantang River which may explain why the tap waters in Hangzhou showed similar pattern with that of the Qiantang River waters. The lack of PFHxS in the tap waters suggests that the tap waters be likely more influenced by the local sources in the north bank of the Qiantang River.

Significant correlations (the significance level $p = 0.05$) between the PFAA concentrations in the surface waters and tap waters from the studied areas were observed (Fig. 6), suggesting the influence of the surface waters on the tapwater with respect to PFAAs. It can be seen that the tap waters can be influenced by surface waters with respect to PFAAs also in other cities such as Suzhou and Shanghai due to the fact that the tap water sources in the region are mainly surface waters. PFHxS was the predominant compound both in Taihu Lake water and the tapwater in Suzhou. It should be noted that some of the surface waters that are not served as the water source for tapwater were correlated with the tapwater, such as West Lake water in Hangzhou, suggesting that the source water of the tapwater supplying plants might not be well protected and separated from contaminated surface waters. The tap water plants may also not remove some PFAA compounds effectively. The Σ PFAAs in the tap water samples from Hai'ning and Hangzhou averaged 71.4 ng/L, which was 35.7% of the average Σ PFAAs in the Qiantang River water (200.1 ng/L), implying that the removal efficiency of PFAAs was about 65% in the local tap water plants.

4. Conclusions

PFAAs were widely detected at relatively high levels in surface waters of textile, leather, and paper making industrial areas in the

Table 1
Comparisons of PFAA concentrations in tapwater and surface water in China and other parts of the World (ng/L).

Sampling sites	Sampling year	Range (Mean) (ng/L)	References
Tapwater			
Hangzhou, China	2015	12.5–175.3 (82.9)	This study
Hai'ning, China	2015	44.3–65.1 (51.4)	This study
Beijing, China	2015	1.4–4.9 (3.2)	This study
Shanghai, China	2015	9.5–45.4 (22.0)	This study
Shanghai, China	2006–2008	PFOS: 7.6; PFOA: 78	Mak et al., 2009
Changshu, China	2015	56.0–155.4 (122.4)	This study
Suzhou, China	2015	11.2–109.9 (55.7)	This study
21 cities in China	2002–2005	PFOS: 0.1–14.8; PFOA 0.1–45.9	Jin et al., 2009
Tokyo, Japan	2012	(19)	Imai et al., 2012
Vietnam	2013–2015	0.00–1.19 (0.31)	Lam et al., 2017
North Rhine, Germany	2013	1.0–42.7	Wilhelm et al., 2010
Italy	2006	PFOS: 1.8–2.9, PFOA: 7.2–8.6	Castiglioni et al., 2015
Bankok, Thailand	2014	0.58–1.15	Tabtong et al., 2015
France	2012	>100	Boiteux et al., 2012
The United States	2009	PFOA: 115	Quiñones and Snyder, 2009
United Kingdom	2008	PFOS: <11–45; PFOA: <24–240	Atkinson et al., 2008

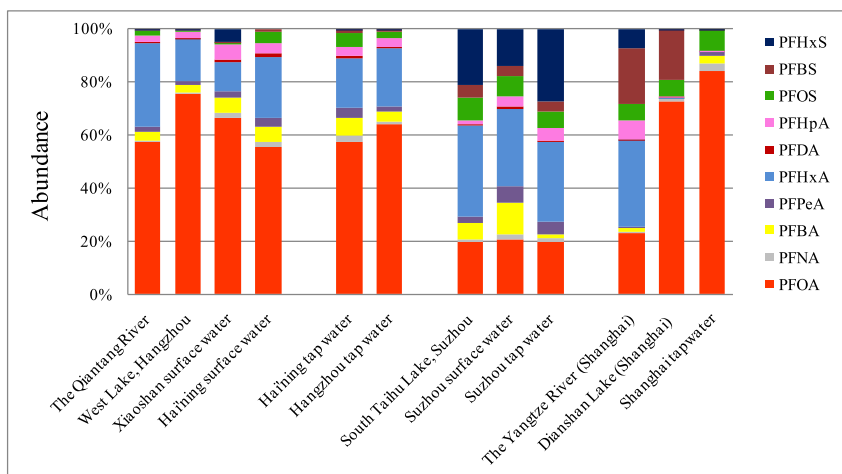


Fig. 5. Comparison of the average compositions of PFASs in surface waters and tap waters from Hai'ning, Hangzhou, Suzhou, and Shanghai.

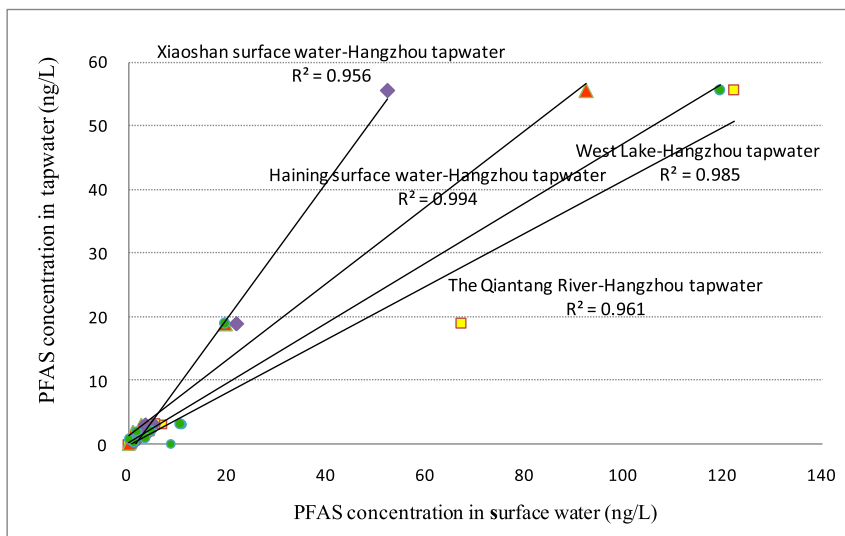


Fig. 6. Correlations between PFAS concentrations in surface waters and tap waters from the studied areas (R denotes the correlation coefficient, $p < 0.05$).

watershed of the Qiantang River and the “Great Hangzhou Area”, i.e. Fuyang, Hangzhou, Xiaoshan, and Hai'ning, which were comparable to the highest PFAA contamination levels in surface waters of China. A unique PFAA compositional feature was observed in these areas characterized by the dominant compound PFOA, followed by PFHxA, and PFBA. There is no much difference between the isomer compositions of PFAAs in leather, textile, and paper industrial areas except for the significant higher PFAA contamination level in the textile industrial area with the occurrence of PFHxS.

The Σ PFAAs in tap waters showed a similar PFAA composition profiles to that of the surface waters and were at a moderate-to-high contamination level that may not pose health risk to the local residents. Good correlations between PFAA concentrations in surface waters and tap waters from the studied areas were observed. The tap waters in Hangzhou and Hai'ning were more influenced by sources in the north bank than in the south bank of the Qiantang River. Tap waters can be influenced by surface waters with respect to PFAAs also in other areas such as Suzhou and Shanghai due to the fact that the tap water sources are mainly surface waters. Some PFAA compounds in the local tap water plants

may not be removed effectively.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2017.06.139>.

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