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

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HIGHLIGHTS
- Perfluorohexanoic acid (PFHxA) was the predominant PFASs in some cities.
- PFOS represented a small proportion of ∑PFASs.
- More than 4000 kg year⁻¹ PFASs are discharged into the East China Sea.

GRAPHICAL ABSTRACT

ABSTRACT
Spatial distributions of perfluoroalkyl substances (PFASs) were investigated in surface waters in Shanghai, Jiangsu and Zhejiang Provinces of eastern China during 2011. A total of 39 samples of surface waters, including 29 rivers, 6 lakes and 4 reservoirs were collected. High performance liquid chromatography/negative electrospray ionization-tandem mass spectrometry (HPLC/(−)ESI-MS/MS) was used to identify and quantify PFASs. Concentrations of PFAS were greater in Shanghai than that in Zhejiang Province. Concentrations of the sum of PFASs (∑PFASs) in Shanghai and Kunshan ranged from 39 to 212 ng L⁻¹, while in Zhejiang Province, concentrations of ∑PFASs ranged from <0.07 to 146 ng L⁻¹. Perfluorooctanoic acid (PFOA) was the prevalent PFAS in Shanghai. In contrast, PFOA and perfluorohexanoic acid (PFHxA) were the prevalent PFASs in Zhejiang Province. Concentrations of perfluorooctane sulfonate (PFOS) ranged from <0.07 to 9.7 ng L⁻¹. Annual mass of ∑PFASs transported by rivers that flow into the East China Sea were calculated to be more than 4000 kg PFASs. Correlation analyses between concentrations of individual PFASs showed the correlation between PFHxA and PFOA was positive, while the correlation between PFHxA and perfluorooctane sulfonamide (FOSA) was negative in Shanghai, which indicated that PFHxA and PFOA have common sources. Principal component analysis (PCA) was employed to identify...
1. Introduction

Because of their characteristics of surface activity, chemical stability and hydrophobic and oleophobic amphiphilic nature, perfluoroalkyl substances (PFASs) during the last half century have been widely used in various processes and products, including production of emulsifiers, surfactants, dust preventive, disposable tableware additives, and fire-fighting foams (Giesy and Kannan, 2001, 2002; Olsen et al., 2005, 2007; Prevedouros et al., 2006; Giesy et al., 2010). Previous studies have documented that widespread application as well as environmental persistence and bioaccumulation of terminal degradation products of PFAS precursors have resulted in global occurrence of PFASs in the atmosphere (Kim et al., 2012), waters (Zushi and Masunaga, 2011), sediments (Naile et al., 2013), not only from urban areas, but from remote areas such as Qinghai-Tibet Plateau (Shi et al., 2010) and polar regions (Cai et al., 2012a,b). Overall, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were the two most often observed and reported PFASs because of their abundant production and wide use in fluoropolymer manufacture (Prevedouros et al., 2006).

In 2009, PFOS and its related compounds were listed in Annex B of the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) (Wang et al., 2009). Then shorter-chain PFASs (carbon chain length less than seven), which have lesser toxic potency than the 8-carbon PFASs (Beach et al., 2006; Buhkre et al., 2013), have been increasingly used. After the phase-out of PFOS-based chemicals (Olsen et al., 2005), a shift from 8-carbon PFASs to the 4-carbon PFBS has been observed in the PFASs in dated cores from Lake Michigan, in North America in the region where 3 M manufactured PFOA and PFOS (Codling et al., 2014). Perfluorobutanesulfonate (PFBS) and perfluorobutanoic acid (PFBA) dominated PFASs in the River Rhine (Möller et al., 2010), while PFBS was the most prevalent PFAS in the Netherlands (Kwadijk et al., 2010). In Japan, PFNA has become the most prevalent PFAS in the Tokyo Bay basin (Zushi et al., 2011). In China, concentrations of some shorter-chain substitutes are increasing in surface waters from various industrial areas, such as perfluorohexanoic acid (PFHxA) in Liaoning Province (Sun et al., 2011) and in Tai Lake in Jiangsu Province (Yu et al., 2013), whereas in Hubei Province PFBS and PFBA were the predominant PFASs (Zhou et al., 2013). Current contaminations of PFASs mainly arise from application of alternatives and consumption of stockpiles of longer-chain PFASs.

The Yangtze River delta, one of the most investigated areas in China, is unique relative to PFASs, because it is located at the junction of eastern coastal developed areas, involving Shanghai and parts of Jiangsu and Zhejiang Provinces. Shanghai, an industrialized, densely populated urban area, is situated where the Huangpu River receives effluents containing PFASs. To date, investigations of PFASs in surface waters of cities around the Yangtze River delta (So et al., 2007; Pan and You, 2010) have focused primarily on PFOA and PFOS, and further comprehensive studies about variation of dominant PFASs and restructure of PFAS patterns are required.

In the present study, concentrations of 17 PFASs were quantified in 39 surface waters, which were collected in eastern China, including 28 rivers, 7 lakes and 4 reservoirs. The objectives of this study were to: (1) determine concentrations, profiles, patterns of relative concentrations and spatial distributions of PFASs in eastern China; (2) identify possible pollution sources in eastern China; (3) calculate discharge loads of PFASs to the East China Sea.
Oasis WAX cartridges to extract 1 L seawater spiked with 400 pg internal standards. PFASs in the upper cartridge accounted for more than 80% of the sum determined from both cartridges. However, there were no internal standards detectable in the lower cartridge, indicating little breakthrough for PFASs with Oasis WAX cartridge. The MDLs were determined by spiking with 400 pg internal standards in 1 L Millipore water which is pre-cleaned with Oasis WAX cartridge. The MDLs were established at a signal-to-noise (S/N) of 10, which ranged from 0.02 ng L\(^{-1}\) (for both PFDA and perfluoroundecanoic acid (PFUnDA)) to 0.14 ng L\(^{-1}\) for PFBA. Overall recoveries ranged from 51 ± 21% for \([^{13}C_4]\)-PFOS to 78 ± 20% for \([^{18}O_2]\)-PFHxS (Table S2). Concentrations were corrected for recoveries of IS in every sample.

3. Results and discussion

3.1. Spatial distributions and compositions of PFASs in eastern China

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

Concentrations of ∑PFASs in Shanghai and Kunshan ranged from 39 ng L\(^{-1}\) to 212 ng L\(^{-1}\) (Table S4), which were comparable with those in Shenyang (Sun et al., 2011), but less than those from Wuhan (Wang et al., 2013) and Fuxin, Liaoning (Bao et al., 2011), and greater than those for Vietnam (Kim et al., 2013) and Tokyo bay, Japan (Zushi et al., 2011) (Tables 1 and S5). In Zhejiang Province, concentrations of ∑PFASs were a less with a mean of 43 ng L\(^{-1}\) and a range of 0.68–146 ng L\(^{-1}\), which were also less than those for Singapore (Nguyen et al., 2011), comparable with Liao River (Yang et al., 2011), but greater than those observed in Seoul and Busan, Korea (Kim et al., 2011) and Huai River (Ye et al., 2013) (Tables 1 and S5). ZJ16 and ZJ17 were collected directly from municipal sewage outfalls at the inner and outer sluice gate and were considered as spot sources, so they were not included in the calculation of the mean and range of Zhejiang Province.

Patterns of relative concentrations of PFASs varied among locations, which indicates different potential sources between Zhejiang and Shanghai. PFOA was the most prevalent compound in samples from Shenyang and Shanghai, accounting for 51–86% of ∑PFASs while PFOA and PFHxA dominated concentrations of ∑PFASs in most industrial locations of Zhejiang Province, which were as great as 80% and 46%, respectively (Fig. 2).

3.2. Sources of PFASs in Zhejiang Province

In Zhejiang Province, we choose 29 sampling sites including four reservoirs, five lakes and twenty river samples to study concentrations and composition of PFASs. In Zhejiang Province, the greatest concentration of the ∑PFASs, 146 ng L\(^{-1}\), which was observed in West Lake (ZJ1) in the city of Hangzhou (Table S3), was greater than those in samples from locations in the river. There are no known discharges because of the area around West Lake is a protected region with no industrial development. However, due to rapid development of tourism, consumption of water in the West Lake scenic area, especially during the wet season when samples were taken, the capacity of the sewage system is exceeded and wastewater can spill out of sanitary sewers and flow into West Lake. Diffuse sources such as urban runoff can also an important potential source (Ahrens, 2011). These sources might be the cause of the observed concentrations of PFASs in West Lake.
In Zhejiang Province PFOA, PFHxS and PFBS were the most frequently detected PFASs. According to the profiles of relative concentrations, locations ZJ1–ZJ11 were predominated by PFOA and PFHxS, followed by PFHxA and PFBS. Concentrations of PFOS were less with a range from <0.07 to 5.0 ng L\(^{-1}\), which are located in West Lake (53 ng L\(^{-1}\)) and Liao River (0.33–44 ng L\(^{-1}\)). The greatest concentration of PFOA in Zhejiang Province, especially location ZJ17, which is located just outside the sluice on the Cao’e River. However, when river water flowed inside the sluice (ZJ16), the concentration of PFOA was 90 ng L\(^{-1}\), with concentrations of other individual PFASs only slightly different. This result indicates that PFHxA has become a replacement for C8 compounds (Meyer et al., 2011; Yu et al., 2013). Zhejiang Province has the largest production of fluorine-based chemicals in China (Fluoroplastics of China, 2011), and the Juhua conglomerate is its leading enterprise. Juhua has developed a new C6-based water and oil repellent furnishing product that does not contain C8 compounds, use of which is likely responsible for the greater concentrations of PFHxA observed in this study (Yu et al., 2013).

Locations ZJ10 and ZJ11 are located in the inlets southwest of Tai Lake (Ch: Taihu), which is the third largest freshwater lake in China. Results of previous studies of Tai Lake (Table 1) indicated that concentrations of PFASs have varied as a function of time. From 2009 to 2011, concentrations of \(\sum\)PFASs have decreased (Qiu et al., 2010; Yang et al., 2011; Yu et al., 2013). Concentrations of PFOS (2.0–2.8 ng L\(^{-1}\)) observed in the study, the results of which are different from those of previous studies where PFOA and PFOS are the two predominant PFASs (Thompson et al., 2011; Yu et al., 2013). The prevalence of PFHxA instead of PFOA suggests a transition in production of PFASs after restrictions for PFOA and PFOS were introduced, such that PFHxA has become a replacement for C8 compounds (Meyer et al., 2011; Yu et al., 2013). Zhejiang Province has the largest production of fluorine-based chemicals in China (Fluoroplastics of China, 2011), and the Juhua conglomerate is its leading enterprise. Juhua has developed a new C6-based water and oil repellent furnishing product that does not contain C8 compounds, use of which is likely responsible for the greater concentrations of PFHxA observed in this study (Yu et al., 2013).

### Table 1: Comparison of concentrations of individual PFASs in surface waters in China.

<table>
<thead>
<tr>
<th>Type</th>
<th>Sampling date</th>
<th>Site</th>
<th>PFOS</th>
<th>PFHxA</th>
<th>PFBA</th>
<th>PFNA</th>
<th>PFDA</th>
<th>(\sum)PFAS</th>
<th>Area description</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake</td>
<td>05/2011–07/2011</td>
<td>West Lake</td>
<td>0.35</td>
<td>53</td>
<td>85</td>
<td>0.50</td>
<td>0.20</td>
<td>146</td>
<td>Urban area</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>05/2011–07/2011</td>
<td>Tai Lake (n = 2)</td>
<td>2.0–2.8</td>
<td>9.4–10</td>
<td>20–23</td>
<td>1.1–1.2</td>
<td>0.42–0.57</td>
<td>7.7–7.6</td>
<td>Lake inlet</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>07/2011</td>
<td>Tai Lake</td>
<td>15</td>
<td>19</td>
<td>56</td>
<td>2.6</td>
<td>1.5</td>
<td>16</td>
<td>Industrial area</td>
<td>Yu et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>02/2009–04/2009</td>
<td>Tai Lake</td>
<td>3.6–394</td>
<td>na(^a)</td>
<td>na(^a)</td>
<td>11–37</td>
<td>&lt;0.8</td>
<td>&lt;0.3</td>
<td>3.9–400</td>
<td></td>
</tr>
<tr>
<td></td>
<td>05/2008</td>
<td>Guanting reservoir</td>
<td>0.2–0.52</td>
<td>&lt;1</td>
<td>0.55–2.3</td>
<td>&lt;2</td>
<td>&lt;0.2–0.23</td>
<td>0.70–3.1</td>
<td>Drinking water source</td>
<td>Wang et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>05/2011–07/2011</td>
<td>Tianpu reservoir</td>
<td>0.07</td>
<td>0.15</td>
<td>1.3</td>
<td>0.17</td>
<td>0.070</td>
<td>2.1</td>
<td>Town area</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>11/2004</td>
<td>Shanghai</td>
<td>12–14</td>
<td>5.0–5.3</td>
<td>230–260</td>
<td>9.0–10</td>
<td>3.3–3.8</td>
<td>&lt;1</td>
<td>Urban area/industry area</td>
<td>So et al. (2007)</td>
</tr>
<tr>
<td></td>
<td>12/2008</td>
<td>Hai River, Tianjin</td>
<td>1.1–7.7</td>
<td>na(^a)</td>
<td>4.7–23</td>
<td>0.29–2.2</td>
<td>12.0–1.0</td>
<td>&lt;1</td>
<td>Urban area/industry area</td>
<td>Pan et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>08/2009</td>
<td>Fuxin</td>
<td>0.28–0.54</td>
<td>na(^a)</td>
<td>27–668</td>
<td>0.43–16</td>
<td>&lt;0.10–21</td>
<td>370–713</td>
<td>Urban area/industry area</td>
<td>Bai et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>09/2009</td>
<td>Shenyang</td>
<td>0.66–16</td>
<td>1.3–37</td>
<td>9.2–25</td>
<td>&lt;1.30–5.2</td>
<td>&lt;1.08–1.2</td>
<td>17–240</td>
<td>Urban area/industry area</td>
<td>Sun et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>09/2009</td>
<td>Hun River, Liaoning</td>
<td>0.40–3.3</td>
<td>1.3–38</td>
<td>1.8–11</td>
<td>&lt;1.30–1.6</td>
<td>&lt;1.08–0.66</td>
<td>&lt;1</td>
<td>Urban area</td>
<td>Sun et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>11/2009–12/2009</td>
<td>Liao River</td>
<td>0.33</td>
<td>na(^a)</td>
<td>11</td>
<td>&lt;0.8</td>
<td>0.3</td>
<td>44</td>
<td>Urban and industrial area</td>
<td>Yang et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>2009</td>
<td>Victoria Harbour, Hongkong</td>
<td>0.030–1.00</td>
<td>0.15–0.97</td>
<td>0.31–1.9</td>
<td>0.032–0.40</td>
<td>0.014–0.31</td>
<td>&lt;1</td>
<td>Urban area</td>
<td>Loi et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>04/2010</td>
<td>Wuhan</td>
<td>52</td>
<td>nd(^b)</td>
<td>81</td>
<td>19</td>
<td>28</td>
<td>204</td>
<td>Urban area/industry area</td>
<td>Wang et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>03/2011</td>
<td>Huai River</td>
<td>0.47</td>
<td>0.68</td>
<td>12</td>
<td>0.91</td>
<td>0.33</td>
<td>28</td>
<td>Industrial area</td>
<td>Yu et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>05/2011–07/2011</td>
<td>Hangzhou Bay</td>
<td>1.0</td>
<td>25</td>
<td>45</td>
<td>0.69</td>
<td>0.31</td>
<td>77</td>
<td>Coastal area</td>
<td>This study</td>
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<tr>
<td></td>
<td>05/2011–07/2011</td>
<td>Quantang River</td>
<td>0.41</td>
<td>31</td>
<td>57</td>
<td>0.66</td>
<td>0.31</td>
<td>97</td>
<td>Urban area</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>05/2011–07/2011</td>
<td>Cohe River</td>
<td>0.24</td>
<td>0.76</td>
<td>4.8</td>
<td>0.54</td>
<td>0.37</td>
<td>90</td>
<td>Middle stream</td>
<td>This study</td>
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<td></td>
<td>05/2011–07/2011</td>
<td>Fenghua River</td>
<td>2.8</td>
<td>2.7</td>
<td>53</td>
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<td>0.48</td>
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<td>Town area</td>
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<td>Yong River</td>
<td>1.6</td>
<td>2.4</td>
<td>3.9</td>
<td>1.0</td>
<td>0.35</td>
<td>53</td>
<td>Town area</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>05/2011–07/2011</td>
<td>Yuyao River</td>
<td>3.4</td>
<td>3.2</td>
<td>37</td>
<td>1.5</td>
<td>0.73</td>
<td>64</td>
<td>Town area</td>
<td>This study</td>
</tr>
<tr>
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<td>05/2011–07/2011</td>
<td>Ou River</td>
<td>0.07</td>
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<td>0.64</td>
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<td>0.050</td>
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<td>Rural area</td>
<td>This study</td>
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<td>Feiyun River</td>
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<td>1.7</td>
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<td>&lt;0.02</td>
<td>3.3</td>
<td>Rural area</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>05/2011–07/2011</td>
<td>Jiao River</td>
<td>5.0</td>
<td>1.0</td>
<td>4.3</td>
<td>0.80</td>
<td>0.33</td>
<td>15</td>
<td>Rural area</td>
<td>This study</td>
</tr>
</tbody>
</table>

\(^a\) na: Not analysed.

\(^b\) nd: Not detected. MDLs were 0.6–8 ng L\(^{-1}\) for all target analytes in water samples according to Wang et al. (2013). MDLs of individual PFASs were not given in the literature.

\(^\dagger\) “…”: Not given in the literature.
sewage and industrial wastewater (Zhang et al., 2013). Different from the situation in Zhejiang Province, in Shanghai and Kunshan (KS1–KS2) only PFOA predominated concentrations of $\sum$PFASs with a mean concentration of 88 ng L$^{-1}$ (Table S4). After PFOA were PFHxS and PFBS, which were detected with lesser ranges of 4.0–16 ng L$^{-1}$ and 4.6–12 ng L$^{-1}$, respectively. PFOS and other individual PFASs also occurred at lesser concentrations. Compared with other industrial areas around the world, Shanghai and Kunshan were more contaminated by PFOA than those in Vietnam (Kim et al., 2013), Germany, Spain, (Llorca et al., 2012), Tokyo (Zushi et al., 2011), France (Labadie and Chevreuil, 2011) and Tianjin (Pan et al., 2011) and Shenyang in China (Sun et al., 2011) (Table S5), but less than those for Wuhan (Wang et al., 2013) and Fuxin (Bao et al., 2011) in China (Table 1). This indicated PFOA was largely used in industrial production in China, and the fluorine chemical industry was likely the main source of PFASs (Xiao et al., 2012; Yan et al., 2012). The large concentration of 212 ng L$^{-1}$ $\sum$PFASs observed at SH1 might be attributable to discharges from wastewater plants (WWTPs) in Shanghai, which have been determined to be the major sources of PFASs to surface water (Sun et al., 2011). Compared with results of a previous study in Shanghai (So et al., 2007), at the location, named SH3 in former study, that is near location SH1 in this study, a decrease of PFOS and PFOA was observed (Table 1), confirming that restrictions for C8 compounds are functioning to reduce releases of C8 chemicals to the environment.

3.4. Mass loadings of PFASs to the East Sea

PFASs are expected to mainly remain in the water column and thus can be transported with riverine flows based on their solubilities and persistences (Boulanger et al., 2005). The area studied is a typical source of PFAS emission in east China. To evaluate the emissions of PFASs from the source area to the coastal waters of China and ultimately to the global marine environment, discharges of PFASs were calculated (Eq. (1); Sun et al., 2011).

\[
\text{Mass flow} = C_{\text{water}} + F_{\text{water}}
\]

where $C_{\text{water}}$ is PFAS concentration in water (ng L$^{-1}$) and $F_{\text{water}}$ is the river flux. For samples for which a particular PFAS could not be detected, a surrogate concentrations equivalent to half of MDLs were used. Mass flow of PFASs in this study just indicated dissolved fraction of PFASs from rivers to the sea, regardless of form of compounds in seawater.

Dissolved concentrations of PFASs, measured at mouths of rivers in each basin were used along with average annual discharges to estimate loads to the East China Sea, without consideration of seasonal differences in discharges (Table 2). The Huangpu and Qiantang Rivers (SH1 and ZJ7) exhibited relatively large mass flows of $\sum$PFASs of 2146 and 1445 kg year$^{-1}$, respectively, to the East China Sea. The Huangpu River transported 1841 kg PFOA year$^{-1}$, followed by Qiantang River and Yong River (ZJ22) with 849 kg year$^{-1}$ and 137 kg year$^{-1}$, respectively (Table 2). A discharge of 461 kg PFHxA year$^{-1}$ came from the Qiantang River, followed by 107 kg year$^{-1}$ from the Huangpu River, which indicates that the Qiantang River contributed more PFHxA to the East China Sea every year. All the rivers studied flow directly into the East China Sea, expect the Huangpu River, which joins the Yangtze River before it finally runs into the East China Sea. Thus, more than 4000 kg of dissolved PFASs were discharged annually into the East China Sea.

In comparison with other rivers in the world, the mass flow of $\sum$PFASs of Huangpu River (2146 kg year$^{-1}$) was greater than those of the Ebro River with a loading of 31 kg $\sum$PFASs year$^{-1}$ (Sánchez-Avila et al., 2010) and the Elbe River with a loading of 113 kg year$^{-1}$ to North sea (Ahrens et al., 2009b), but lesser than those of the Po River in Italy, which had a loading of 2628 kg $\sum$PFASs year$^{-1}$ (Loos et al., 2008). Alternatively, mass loadings of other individual PFASs in present study were less than PFOA and PFHxA, especially for PFOS. The flux of PFASs of the Hanjiang River in Wuhan, China was 69.8 m$^3$ s$^{-1}$, but the great concentration of PFOA in waters of the Hanjiang River resulted in a relatively great flux of 130 kg PFOS year$^{-1}$ (Wang et al., 2013), which was greater than any river in present study. Mass flow evaluation is essential to determine the pollution of a river and to the ocean rather than the concentration or the flux singly.

3.5. Correlations between concentrations of individual PFASs and influence factor analysis

Relationships among PFASs and identification of sources of PFASs in surface waters of eastern China were investigated by use of pairwise correlations and factor analyses. Two regions, Shanghai and Kunshan (n = 10) and Zhejiang Province (n = 29),

![Fig. 2. Profile of relative contributions of individual PFASs to sum-PFASs in surface waters of eastern China.](image_url)

**Table 2**

Estimated flux of dissolved PFASs in selected rivers of eastern China (kg year$^{-1}$).

<table>
<thead>
<tr>
<th>Name</th>
<th>Discharge (m$^3$ s$^{-1}$)</th>
<th>PFOS</th>
<th>PFOA</th>
<th>PFNA</th>
<th>PFHxA</th>
<th>$\sum$PFAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huangpu River</td>
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<td>1841</td>
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<td>Caö River</td>
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<td>Yong River</td>
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<td>1.8</td>
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<tr>
<td>Yuyao River</td>
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<td>61</td>
<td>2.5</td>
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<td>2.2</td>
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<td>6.8</td>
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<td>13</td>
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* $\sum$PFAS includes PFBS, PFHxS, PFHpS, PFOS, PFBA, PFPA, PFHxA, PFHpA, PFNA, PFDA, PFUnDA and FOSA.
were analyzed by use of Spearman rank correlation analysis (Table S6). In Zhejiang Province, except for FOSA, most of the PFASs were positively correlated, regardless of whether they were PFSAs or PFCAs, which indicates common sources for most of the PFASs. However, for Shanghai and Kunshan, no correlations were found between concentrations of PFASs (C4, C6–C8), but strong correlations were observed among longer-chain PFCAs (>C6). PFOA came primarily from industrial manufacture while PFHpA, PFNA, PFDA and PFUnDA were possibly from degradation of fluorotelomer alcohols (FTOHs) (So et al., 2007; Möller et al., 2010) because concentrations of those compounds were less in the study area. In the Shanghai-Kunshan region, PFHxA was positively correlated with PFOA \((r = 0.661, p = 0.05)\) but negatively correlated with FOSA \((r = -0.677, p = 0.05)\). Therefore, it is likely that PFHxA and FOSA were released from different sources. Results of Principle Component Analyses (PCA) also shows the same result (Fig. 3). Two principal components were extracted from the composition data, from Zhejiang Province, Shanghai and Kunshan \((n = 39)\). Longer-chain PFCAs (C > 8) were positively loaded together into the first principal component (PC1). Concentrations of PFHxA were significantly and positively associated with the second principal component (PC2), while concentrations of FOSA were negatively loaded to PC2 (Fig. 3). Results of previous studies have shown that FOSA was related to degradation of precursors like N-ethylperfluorooctane sulfonamide (N-EtFOSA) and perfluorooctane sulfonamide acetate (FOSAA) (Rhoads et al., 2008; Plumlee et al., 2009). Similar to PFOA, PFHxA was probably released directly from industries during manufacture or use, a conclusion which is consistent with those of previous studies, which indicating that greater concentrations of PFHxA or PFOA precursors in WWTPs probably came from industrial sources (Xiao et al., 2012). The result was agreement with the conclusion that PFHxA was used as new material in manufacture industry of Zhejiang Province, China.

4. Conclusions

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

Acknowledgments

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Appendix A. Supplementary material

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References


