Research Article

Distribution and Bioaccumulation of Perfluoroalkyl Acids in Xiamen Coastal Waters

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Since perfluoroalkyl acids (PFAs) are widely used and harmless to organisms, they have attracted great attention in recent years. The distribution of PFAs in the oceans all around the world is well documented. However, the study of PFAs in Xiamen could be a beneficial complement, for its unique geologies of no rivers that originate from other cities to influence the concentration of PFAs in this area. In this paper, six PFAs were analyzed in water, sediments, and organisms from both freshwater and seawater and the bioaccumulation factors (BAFs) were calculated with the quantity of PFAs in different trophic levels of aquatic organisms. The results showed that the ΣPFA concentrations ranged from 7.66 to 11.98 ng L⁻¹ for seawater samples and from 2.12 to 8.61 ng L⁻¹ for freshwater. The concentration of ΣPFAs in sediments was 7.43–12.89 ng g⁻¹ and 4.53–5.80 ng g⁻¹ in seawater and freshwater, respectively. The PFA concentration in water is highly positive correlated with the PFA concentration in sediments (R² = 0.85). The calculated bioaccumulation factors (BCFs) were 6412–14254 L kg⁻¹ and 2927–7959 L kg⁻¹ for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonates (PFOS), respectively. PFOA seems more bioaccumulative than PFOS in seawater. The results illustrated the PFA pollution in the Xiamen sea area, and it is useful for the protection and control of the organic pollutants in this area.

1. Introduction

Perfluorinated acids (PFAs) have emerged as a new class of global environmental pollutants and have a wide range of industrial applications, such as fire-fighting foams, pesticides, and consumer applications including surface coatings for carpets, furniture, and paper products [1]. The unique physicochemical properties of perfluorinated compounds, such as high surface activity, thermal stability, and amphipathicity, are responsible for their industrial value, but they also contributed to the compounds’ persistence in the environment and accumulation in biota [2, 3]. PFAs persist in the environment as persistent organic pollutants, but unlike PCBs, they are not known to degrade by any natural processes due to the strength of the carbon-fluorine bond [4, 5].

Due to their high water solubility, PFAs are ubiquitous in various kinds of waters and the aqueous phase is considered as a major sink for PFAs [4–7]. About 40 perfluorinated compounds (PFCs) have been found in ocean water collected from a number of locations, including remote marine locations such as the Arctic and the Antarctic Oceans [8–12].

Many researchers have investigated the pollution of PFCs in major rivers, lakes, reservoirs, and other environments in China and obtained relatively comprehensive pollution situation of PFCs in freshwater environment [13–16]. Studies on PFAs pollution in marine environment of China mainly include the reports on PFA pollution in sediments in the East China Sea, Yellow Sea, and Bohai Sea [17]. In addition, there are also some reports on the amount of PFAs in offshore seawater and sediments in Dalian [10], Shenzhen [18], and Wenzhou [19], as well as reports on the
pollution situation in the estuaries of the Yangtze River, Huangpu River, and Pearl River [20, 21]. Survey shows that nearly all samples have different concentrations of PFAs detected. Generally, compared with other parts of the world, PFAs pollution in China is in the intermediate level among the world. As we know, the aqueous phase is considered as a major sink for PFAs, especially in the oceans. Considering the very long coastline and broad maritime territory of China, the research studies about the distribution of PFAs in the ocean are obviously insufficient. The objective of this research is to study the distribution of PFAs in Xiamen coastal waters. The water, sediment, and organism samples were collected from different sampling sites in Xiamen. In addition, the concentrations of PFAs of several organisms were analyzed, and the bioaccumulation factors were calculated. The purpose of this study is to support basic information about the pollution of PFAs in Xiamen coastal water for the risk assessment and control of PFAs.

2. Materials and Methods

2.1. Chemicals. PFOS (98%) was purchased from Tokyo Chemical Industries (Tokyo, Japan); PFOA (96%), perfluorononanoic acid (PFNA, 97%), perfluorodecanoic acid (PFDA, 98%), perfluoroundecanoic acid (PFUnA, 95%), and perfluorododecanoic acid (PFDoA, 95%) were obtained from Acros Organics (New Jersey, US), and a purity corrected equimass stock standard solution containing these perfluorinated acids was prepared in a 80:20 (v/v) methanol/water solution with the concentration of 200 mg·L⁻¹ for each PFAs. The methanol was purchased from J. T. Baker (chromatography grade, Phillipsburg, NJ, USA). [1,2,3,4-13C₄]Perfluorooctanoic acid (MPFOA) (purity > 99%) was obtained from Wellington Laboratories (Guelph, Canada), and it was used as an internal standard. Ammonium acetate (98%), methyl-tert-butyl ether (MTBE, 99.5%), and tetrabutylammonium hydrogensulfate (TBA) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, US), and they were used to extract PFAs from aquatic organisms.

2.2. Sample Collection. Six surface seawater samples were collected from Xinglin Bay, Fenglin, Zhenzhu Bay, Gulf Park, Convention Center, Wuyuan Bay, and Jimei Bridge (Figure 1). Four freshwater samples were collected from Bantou Reservoir (two samples: one is from the tail and one is from the middle of the reservoir), Beixi River, and Jiangdong Reservoir (Figure 1). Samples were collected using a clean stainless steel grab sampler and stored in 1 L polypropylene containers. About 1 kg sediments were collected at each site by the clean stainless steel grab sampler and stored in 1 L polypropylene containers. The samples were extracted within 24 h after collection.

Aquatic organisms, including crab, oyster, hermit crab, fish, and kelp, were collected from Jimei Bridge, Fenglin, Wuyuan Bay, Haian Bay, and Bantou Reservoir. Since the organisms were difficult to sample, it took almost one month to collect all of them. So the earlier collected organisms were stored at −20°C until analysis. Fish were caught by a fishing net, and all species were coastal fishes.

2.3. Extraction and Analysis of PFAs. The PFAs in sediments and organisms were extracted by the ion-pairing agent extracted method with some modifications [22–24]. A total of 2 mL of Na₂CO₃ (0.25 M), 1 mL of the ion-pairing agent tetrabutylammonium hydrogenosulfate (0.5 M, adjusted to pH 10), 2 mL of MTBE, and 100 μL (10 ng) of MPFOA (as an internal standard) were added into the centrifuge tubes containing the samples in turn. These tubes were shaken vigorously by an oscillator with the speed of 150 rpm for 12 h and then sonicated for 30 min, followed by centrifugation to isolate the organic phase. The MTBE supernatant was collected in a separate polypropylene tube. This extraction process was repeated twice except the shaken time was reduced to 2 h for the second time. The supernatants were combined and blown to dryness under high-purity nitrogen gas, and the analytes were dissolved in 1 mL of 80:20 (v/v) methanol: water solution. The extraction of water samples was similar to that described before [25]. The key step is the
filtration of water samples by 10 g solid-phase extraction (SPE) C18 cartridges.

PFCs, including PFOA, PFNA, PFOS, PFDA, PFDoA, and PFUnA, were analyzed by liquid chromatography-tandem mass spectrometry (LC-MS/MS; Dionex Ultimate 3000 and Applied Biosystems API 3200) in the electrospray negative ionization mode. The methods used in our previous study [26] and those used by Martin et al. were modified to analyze PFA in this study [27]. In brief, a 10 μL aliquot of sample was injected into a 4.6 × 150 mm Acclaim 120 C18 column. The mobile phase was 5 mM ammonium acetate and methanol for tubes A and B, respectively, and the gradient eluting procedure was adopted with a flow rate of 1 mL·min⁻¹. In brief, the mobile phase gradient was ramped from 70% to 95% methanol in 4 min, held at 95% methanol for 3 min, and then ramped down to 70% methanol in 3 min.

2.4. Quality Assurance and Quality Control (QA/QC). The concentrations of all target analytes were quantified from calibration curves drawn using external standards, and the correlation coefficients of the standard curves were higher than 0.98. The limits of quantification (LOQs) were defined as the lowest amount of the PFA concentrations that can be quantitatively determined with a signal-to-noise ratio greater than 7, and the deviations were within ±20% from theoretical values of the duplicate injection. The LOQs of the target chemicals were in the range of 0.01–0.05 ng·mL⁻¹, and the corresponding detection limits for biological samples were 0.05–0.10 ng·g⁻¹ wet weight. Concentrations below the LOQ were set to zero.

The recoveries of PFAs and the internal standard (MPFOA) in water and biological samples ranged from 82% to 93%. Polypropylene or polyethylene containers were used for all stock solutions and test vessels, and glass and Teflon containers were avoided due to the sorption of PFAs on them. The results showed that the PFAs were not detected in blanks.

2.5. Data Processes. One-way analysis of variance and Tukey’s honestly significant difference test were performed using PASW statistic 18.0 for Windows (SPSS). The graphs were drawn by Origin Pro 8 and Microsoft Excel 2016.

3. Results and Discussion

3.1. PFA Distribution in Water. All six PFAs were detected in both freshwater and seawater samples (Table 1). The ΣPFA concentrations ranged from 7.66 to 11.98 ng·L⁻¹ for seawater samples and from 2.12 to 8.61 ng·L⁻¹ for freshwater. In addition, only PFOA, PFOS, and PFNA were detected in Bantou Reservoir and Jiangdong Reservoir. PFos was the predominated PFA with its contribution ranging from 15% to 45%, followed by PFOA, with its contribution ranging from 11% to 18% (Figure 2). PFAs such as PFOS, PFHS, PFOA, and PFOSA have been found in ocean water collected from a number of locations, including remote marine locations such as the Arctic and the Antarctic Oceans. The concentration of PFAs in Xiamen coastal water is in the middle level when compared to other bays. For example, the PFOA and PFOS concentration ranges from 0.9 to 1.4 ng·L⁻¹ and 1.07 to 5.37 ng·L⁻¹; however, it ranges from 0.73 to 5.5 ng·L⁻¹ and 0.09 to 3.1 ng·L⁻¹ in Hong Kong, 0.24 to 320 ng·L⁻¹ and 0.04 to 730 ng·L⁻¹ in Korea, 0.17 to 37.55 ng·L⁻¹ and <0.10 to 2.25 ng·L⁻¹ in Dalian, and 1.8 to 192 ng·L⁻¹ and 0.34 to 58 ng·L⁻¹ in Tokyo, respectively [7, 9, 10, 25, 28, 29].

In most cases, the concentration of PFAs in seawater samples and freshwater samples is close to each other, and they are below 10 ng·L⁻¹, except the sample from Wuyuan Bay. The sampling site of Wuyuan Bay is close to a municipal sewage outfall. As we know, the PFA is one kind of synthetic compounds, and its pollution is all comes from human activities. So maybe that is the reason why the concentration of PFAs in Wuyuan Bay is higher than other sampling sites. In fact, the other sampling locations that have a relatively higher concentration, such as Fenglin and Xinglin Bay, were all near the domestic sewage outfalls or industrial effluents outfalls. In addition, as described above, only 3 PFAs were detected in two reservoirs. The results may attribute to the reason that these reservoirs are drinking water sources, and they have been protected for several years. So, little pollutants were introduced to the reservoirs and led to the low concentration of PFAs.

The special distribution of 9 PFCs from the East to South China Sea was investigated by Cai et al. The results showed that the ΣPFC concentrations ranged from 0.13 ng/L to 3.320 ng/L, with PFOA (0.037–1.54 ng/L), PFBS (0.023–0.94 ng/L), and PFHpA (0–0.42 ng/L) as dominant compounds [30]. These samples were gathered in coastal waters along Shanghai, Ningbo, Taizhou, and Xiamen and along coastal cities of Guangdong Province. The relatively lower PFC concentration may ascribe to the sampling location when compared to this study. The water samples were collected by the research vessel Snow Dragon a few kilometers way from the coast, but in this study, they were collected about 100 m away from the coast. Since the PFCs were man-made pollutants, their concentrations decrease from the coast to the open sea area.

In addition, the PFC concentrations in Jiulong River have been investigated, and the results showed that total content of 17 PFCs in the water sample from Jiulong River watershed estuary was in the range of 5.31–463.16 ng/L in dry season, 3.14–155.16 ng/L in medium season, and 3.57–42.96 ng/L in wet season [31]. Jiulong River is close to Xiamen, and the relatively higher PFC concentration in Jiulong River watershed estuary indicated that that the PFCs could migrate along the river and accumulate in the lower course of river.

The concentration of PFAs from seawater samples is higher than the concentration from freshwater samples, and the only exception is the sample from Beixi Channel. Beixi Channel is an aqueduct made by concrete. The relatively high concentration of PFAs may attribute to the construction material. Otherwise, the water in Beixi Channel comes from JiuJong River, which has been polluted by various kinds of pollutants.
3.2. PFA Distribution in Sediments. The concentration of ΣPFAs in sediments of seawater is ranged from 7.43 to 12.89 ng·g\(^{-1}\) (Table 2). Obviously, the less polluted sampling sites, reservoirs, have the lowest concentration of PFAs. The ΣPFA concentration from the sediments of the Daliao River system in northeast China were determined in the range of 0.29–1.03 ng·g\(^{-1}\) dry weight, and the concentrations of PFOS and PFOA, dominant PFA contaminants in sediment samples, were ranging between <LOQ and 0.37 ng·g\(^{-1}\) dry weight and from <LOQ to 0.17 ng·g\(^{-1}\) dry weight, respectively [32]. However, the ΣPFA concentration (C2–C14) in sediments from Shanghai is in the range of 62.5–276.9 ng·g\(^{-1}\) [33]. Lin et al. has investigated the sediment from the Science Park of Taiwan, and the results showed that, in sediment samples, predominant contaminants were PFOS (1.5–78 ng/g), PFOA (0.5–5.6 ng/g), and perfluorododecanoic acid (PFDoA) (n.d.-5.4 ng/g) [34]. Generally speaking, when compared to other sediments, the PFA concentration levels in Xiamen are in a relatively lower level.

As shown in Figure 3, the PFA concentration in water is highly positive correlated with the PFA concentration in sediment, with the correlation coefficient as high as 0.85. It means that the PFAs could migrate between water and sediment, and the migration has a significant linear correlation. According to the previous studies, the major factor that controls the migration and transportation is the organic matter in water and sediments [22, 35].

3.3. PFA Distribution in Organisms. As shown in Table 3, all six PFAs were detected in the organism in Xiamen both from seawater and freshwater. The total concentration of PFAs ranges from 7.68 to 17.56 ng·g\(^{-1}\). It is obvious that the organism from Gulf Park and Wuyuan Bay have the relatively higher PFA concentration. Based on above results, we know that the water and sediment samples from Gulf Park and Wuyuan Bay also have relatively higher PFA concentrations. It seems like that the PFA concentration in organisms correlated with the concentration in the environment where they are living in.

According to previous studies, PFOA and PFOS are always the dominant pollutants of PFAs. In the muscle samples of fish from the Keya River and the Keelung River in

### Table 1: Distribution of PFAs in surface waters around Xiamen.

<table>
<thead>
<tr>
<th>Location</th>
<th>Temperature (°C)</th>
<th>Sampling depth (m)</th>
<th>n</th>
<th>ΣPFAs (ng·L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Seawater</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xinglin Bay</td>
<td>18.5</td>
<td>0.2</td>
<td>3</td>
<td>8.36–8.73</td>
</tr>
<tr>
<td>Fenglin</td>
<td>18.8</td>
<td>0.2</td>
<td>3</td>
<td>8.77–9.96</td>
</tr>
<tr>
<td>Zhenzhu Bay</td>
<td>17.9</td>
<td>0.2</td>
<td>3</td>
<td>7.66–7.77</td>
</tr>
<tr>
<td>Gulf Park</td>
<td>18.2</td>
<td>0.2</td>
<td>3</td>
<td>7.98–8.26</td>
</tr>
<tr>
<td>Convention Center</td>
<td>18.1</td>
<td>0.2</td>
<td>3</td>
<td>7.68–7.79</td>
</tr>
<tr>
<td>Wuyuan Bay</td>
<td>18.5</td>
<td>0.2</td>
<td>3</td>
<td>9.86–11.98</td>
</tr>
<tr>
<td>Jimei Bridge</td>
<td>18.4</td>
<td>0.2</td>
<td>3</td>
<td>7.99–8.32</td>
</tr>
<tr>
<td><strong>Freshwater</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bantou Reservoir (middle)</td>
<td>19.3</td>
<td>0.2</td>
<td>3</td>
<td>2.12–2.36</td>
</tr>
<tr>
<td>Bantou Reservoir (tail area)</td>
<td>19.1</td>
<td>0.2</td>
<td>3</td>
<td>2.96–3.52</td>
</tr>
<tr>
<td>Jiangdong Reservoir</td>
<td>18.8</td>
<td>0.2</td>
<td>2</td>
<td>3.16–4.24</td>
</tr>
<tr>
<td>Beixi Channel</td>
<td>18.1</td>
<td>0.2</td>
<td>2</td>
<td>8.01–8.61</td>
</tr>
</tbody>
</table>

Figure 2: Concentration of six PFAs in water samples from Xiamen (the concentration of PFAs represents the mean value).
Taiwan, PFOS accounted for 76–84% and 55–64% of all PFAAs, respectively, and the concentration of PFOA is in the second position [36]. However, in this study, the concentration of PFOA and PFOS are only a little higher than another 4 PFAs. The concentration of PFOS in mussels and oysters from south China and Japan was from 0.113 to 0.586 ng·g$^{-1}$·ww [37].

Other studies reported the concentration of PFOA and PFNA in mussels from a tidal flat area of Ariake Sea in Japan is 9.5 and 1.6 ng·g$^{-1}$·ww [38]. Generally speaking, the reported PFA concentrations in oysters were in the same magnitude, and the reason may ascribe to the similar pollution situation.

The concentration of PFOS in the fish from Keya River and Keelung River was 1,828 and 113 ng/g, respectively, which a thousand and a hundred times of the concentration in the fish from Bantou Reservoir in this study. Schuetze et al. have investigated the concentration of PFOS and PFOA in wild fish caught from different German waters, and the results showed that PFOA was not found in any of the investigated samples above the limit of quantitation of 0.27 μg·kg$^{-1}$·fw, whereas PFOS was found in the filet samples caught from densely populated regions at levels between 8.2 and 225 μg·kg$^{-1}$·fw [39].

As shown in Table 4, the BCF of some organisms in Xiamen freshwater and seawater was listed. The values of...
BCF were calculated with the concentration of PFAs in organisms and the water where they live in. The calculated BCF values of PFOS were at the same order of magnitude with the values from literatures. The reported BCF value of PFOS is $4.50 \times 10^2$ in fathead minnow [40], $1.10 \times 10^3$ in rainbow trout [27], and $1.8 \times 10^3$ in zebrafish [41]. However, the BCF of PFOA in this study is much higher than that reported before. According to the literature, the BCF of PFOA is 4 in rainbow trout [41] and 3.1–9.4 in carp [9].

The previous studies indicated that only the PFAs with the carbon chain length more than 7 could accumulate in organism, and the BCF increases with the increasing carbon chain length [42]. The significant differences of the BCF value of PFOA between this study and reported values may attribute to the difference of water concentration of PFOA. The reported BCF values of PFOA were obtained from experiment that the water concentration of PFOA was set in the level of microgram per liter. However, the value in this study is calculated by the concentration of organisms and the natural water where they live in, and in most cases, the water concentration of PFOA is in nanograms per liter. Therefore, the significant difference of the PFA concentration in water leads to the significant difference of the BCF value. In addition, the environmental factors, like dissolved organic matter or salinity [43], and the different chain length of PFAs could both affect the bioaccumulation of PFAs [44]. So the data from the other area are just used as a reference.

### 4. Conclusion

All six PFAs were detected in water, sediments, and organisms from both freshwater samples and seawater samples. The ΣPFA concentrations ranged from 7.66 to 11.98 ng·L$^{-1}$ for seawater samples and from 2.12 to 8.61 ng·L$^{-1}$ for freshwater. The concentration of ΣPFAs in sediments was 7.43–12.89 ng·g$^{-1}$ and 4.53–5.80 ng·g$^{-1}$ in seawater and freshwater, respectively. The PFA concentration in water is highly positive correlated with the PFA concentration in sediments ($R^2 = 0.85$). The calculated bioaccumulation (BCF) was 6412–14254 L·kg$^{-1}$ and 2927–7959 L·kg$^{-1}$ for PFOA and PFOS, respectively. PFOA seems more bioaccumulative than PFOS in seawater.

### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

### Conflicts of Interest

The authors declare that they have no conflicts of interest.

### Acknowledgments

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