Sediment–water distribution of perfluorooctane sulfonate (PFOS) in Yangtze River Estuary

Gang Pan*, Chun You

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China

PFOS may be largely scavenged to the sediment in estuaries due to the dramatic change in salinity during its transport from lands to oceans.

A R T I C L E   I N F O

Article history:
Received 9 October 2009
Received in revised form 23 December 2009
Accepted 10 January 2010

Keywords:
Perfluorooctane sulfonate
Distribution
Salinity
Sediment
Estuary

A B S T R A C T

Analysis of Perfluorooctane sulfonate (PFOS) distribution in water and sediment in Yangtze River Estuary showed that the estuary was a sink for PFOS. Salinity was an important parameter in controlling the sediment–water interactions and the fate or transport of PFOS in the aquatic environment. As the salinity ($S_{w}$) increased from 0.18 to 3.31, the distribution coefficient ($K_d$) between sediment and water linearly increased from 0.76 to 4.70 L g$^{-1}$. The study suggests that PFOS may be carried with the river water and transported for long distances before it reaches to the sea and largely scavenged to the sediment in the estuaries due to the dramatic change in salinity.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Over the last half-century, there has been a surge in the industrial use of perfluorooctane sulfonate (PFOS). PFOS is chemically and thermally stable, and is considered to be the terminal degradation product of many perfluorochemicals (PFCs) (Development, 2002). Considerable concentrations of PFOS have been detected in wildlife (Kannan et al., 2001; Wang et al., 2008) and humans (Kannan et al., 2004; Yeung et al., 2006). Owing to the potential bioaccumulation and the possible negative impact on the total environment and ultimately humans (Beach et al., 2006), understanding the pathway and investigating the environmental fate of PFOS are urgent.

A number of hypotheses have been proposed on the ubiquity of PFOS, such as indirect route, via degradation of volatile precursor chemicals (Stock et al., 2007; Young et al., 2007) and direct route via oceanic transport of the PFOS itself (Yamashita et al., 2008). The global industry emissions are the major source of PFOS, and deep oceans have been suggested as one of the sinks of PFOS (Prevedouros et al., 2006). River is an important pathway for the transport of PFOS from lands to oceans. The partitioning of PFOS between water and suspended sediment particles is crucial for understanding the transport/transform mechanism of PFOS in the environment. Previous studies indicated that PFOS could sorb strongly to sediment when the environmental parameters such as pH, ionic strength and co-solvent were suitable (Higgins and Luthy, 2006; Johnson et al., 2007; Pan et al., 2009). Hydrophobic partition, static attraction, ion-exchange and salting out effect are presumed to be important mechanisms affecting the sorption process (Higgins and Luthy, 2006; Johnson et al., 2007; Pan et al., 2009). The authors have studied the sorption and desorption of PFOS on suspended sediment particles at different salinity in previous studies, which suggested that the increase of salinity would enhance the sorption of PFOS on sediments and also increase the fraction of resistant desorption from the sediment (You et al., in press). It is reasonable to speculate that PFOS may be scavenged into the sediment in estuaries where a sharp increase of salinity exists. However, there has been no report to confirm this speculation before.

As the longest river in China, Yangtze River flows into East China Sea in Shanghai. Saltwater intrusion and organic pollutants are the major causes to water pollution in these areas (Hu et al., 2004). Seawater intrudes into the Yangtze River Estuary in low flow season, which changes the salinity under different hydrological conditions. Reports on the pollution profiles of Yangtze River Estuary revealed that the estuary was the major depositor of many pollutants (Liu et al., 2003; Shen et al., 2006). Studies showed that the concentration of PFOS are in the range of 0.62–14 ng L$^{-1}$ in Yangtze River (So et al., 2007), the concentration was 52.6 ng L$^{-1}$ in the surface seawater from Shanghai (Wei et al., 2007a) and even...
7.6 ng L⁻¹ in the tap water in Shanghai (Mak et al., 2009). Consequently, to study the salinity dependent PFOS distribution in the Yangtze River Estuary may reveal important mechanism in understanding the fate and transport pathways of PFOS during the land-ocean interaction.

Here, we determine the effect of salinity on the sorption of PFOS and its control on the distribution between the water and sediment in the estuary. Quantitative determinations of PFOS in water and sediment samples of Yangtze River Estuary are attempted. The distribution coefficient (Kd) of PFOS between water and sediment is drawn to analyze the effects of salinity on the distribution and fate of PFOS. Effects of other environmental parameter such as pH and sediment compositions including sediment organic matter and inorganic fractions on the sorption are also studied.

2. Materials and methods

2.1. Standards and reagents

Heptadecafluorooctane sulfonic acid potassium (PFOS) (prumur, ≥98% (T)) and ammonium acetate (≥95.0%) were purchased from Fluka (Milwaukee, WI, USA). Sodium perfluoro-[1,2,3,4]-[13C]octanesulfonate (MPFOS) (99%, 50 mg/mL solution in methanol) was purchased from Wellington Laboratories (Canada). HPLC-grade methanol and acetonitrile were supplied by Fisher Scientific (Leicestershire, UK). Milli-Q water prepared by Millipore (Boston, USA) was used throughout the experiment. All the other reagents used in the experiment were of analytical grade.

2.2. Water and sediment sampling

Samples of water and sediment were collected in Nov. 2008 (low flow season of Yangtze River) from Yangtze River Estuary, China. The sampling locations were distributed in the North harbor, the North bank and the South bank of the estuary respectively (Fig. 1). Water samples were collected from each location using a stainless steel bucket, which was precooled using methanol, Milli-Q water, and the water from specific location. The water samples were characterized using water quality survey instrument (556 Handheld Multiparameter, YSI, USA). Samples were stored in polypropylene (PP) bottles with narrow mouth at 4°C for 4 h to eliminate moisture. The target sample was then dried in a dessicator and then centrifuged at 3000 rpm for 10 min. The supernatant was collected in a precleaned 50 mL PP bottle, and the residual sediment was followed by further treatment. 1.7 mL mixture of 9:1 (v/v) methanol and 1% acetic acid was added to the tube, processed using ultrasonic at 60°C for 15 min, and then centrifuged at 3000 rpm for 10 min. The supernatant was collected and added to the PP bottle mentioned above. These operations were repeated three times. In order to enrich the analyte and remove the acetic acid, salts, and potential matrix interferences, the extracted solution was loaded to SPE cartridges. All the prepared solutions were stored at 4°C prior to PFOS analysis. Extracted solution was transferred to 100 µL polyporopylene insert with polymer feet in 2-mL HPLC/GC auto sampler vial.

Concentrations of PFOS in water and sediment samples were analyzed by High-Performance Liquid Chromatography/Hybrid Quadrupole Time-of-Flight Mass Spectrometer (HPLC/Q-ToF MS). Separation of the analyte was performed by an Alliance 2695 (Waters, USA), interfaced with a quadrupole time-of-flight mass spectrometer (Micromass, Manchester, UK) with a Z-spray ESI source working in negative mode. A 10 µL aliquot of extract was injected into a reversed-phase C18 column (2.1 mm × 50 mm, packed with particle size of 5 mm) (Waters, USA) with 10 mmol L⁻¹ ammonium acetate and methanol in 55:45 (v/v) as the mobile phases at a flow rate of 0.2 mL/min. The mass tune employed the optimized parameters described by Guo et al. (2008). The mass spectrometer parameters were optimized to transmit the [M⁻] ion for PFOS and MPFOS using atmospheric pressure ionization, operated in the electrospray negative ion mode. PFOS and MPFOS ion was monitored using selected reaction monitoring for quantitative determination.

2.4. Quality assurance and control

Spike and recovery experiments were performed to determine the precision and accuracy of the extraction and the analytical procedures. Procedural blanks test was conducted to detect the procedure error; the concentrations of PFOS were all below the limit of detection. These results showed that the preparation and analytical procedure did not introduce any impurities. The method recovery test was conducted by adding 10–100 ng L⁻¹ standard solution. The recovery rates were in the range of 95.3–97.6%. These data meant there was little loss of PFOS in the extract procedure.

Standard solutions containing PFOS and MPFOS analyte were used for calibration. The standard addition experiment was performed by adding 2–50 ng L⁻¹ standard PFOS to the samples. Method recovery rate ranged from 95.25% to 114.72%, and relative standard deviation (RSD) ranged from 0.40% to 10.23%. These results showed acceptable stability of the samples over the course of analysis. The limits of quantification (LOQ) signal to noise ratio — 15.32) for sediments were 0.05 ng g⁻¹ for sediment (dry weight), and 0.50 ng L⁻¹ for river water. The limit of detection of the instrument used for the standard PFOS solution was 0.2 µg L⁻¹ and was 0.5 µg L⁻¹ for water and sediment samples respectively.

3. Results and discussion

3.1. Water and sediment characterisation

The characterisation results on water and sediment samples were presented in Table 1. The salinity of the sampling waters had three grades, which were 0.14–0.18, 2.36 and 3.31, respectively. Locations BZ and BL had the lowest salinity as freshwater, while location JB had the highest salinity. The total organic carbon of sediment samples ranged from 5.89 to 8.34%. The inorganic fractions were greater than 90% in weight, which were mainly clays, silts and sands.

3.2. Concentration of PFOS in water

The measured PFOS concentration in water samples were presented in Table 2. The highest concentration of PFOS was found in the sample collected at BZ (703 ng L⁻¹). Samples from BL also had...
a relatively high concentration of PFOS (144 ng L\(^{-1}\)). Except the high value at location BZ, the PFOS levels detected for other sampling locations were comparable with values reported in Great Lakes (21–70 ng L\(^{-1}\)) (Boulanger et al., 2004) and in sixteen Japanese rivers (0.2–157 ng L\(^{-1}\)) (Saito et al., 2003). The PFOS values investigated in this study were much greater than that detected in Huangpu River (0.62–14 ng g\(^{-1}\)) (So et al., 2007).

The sampling site of BZ is located in Baozhen Port, which serves as a freight terminal and passenger wharf. The area received significant amount of domestic sewerage from the nearby town. It was reported that domestic sewage contains high levels of PFOS (Hekster and Voogt, 2003) and the water quality alongshore was poorer than that in the middle of the river in Yangtze River Estuary (Bochang and Huiyan, 2005). The observed high value of PFOS in BZ was owing to the local pollution.

### 3.3. Concentrations of PFOS in sediments

Measured PFOS levels in sediment samples were presented in Table 2. The values ranged between 72.9 and 536.7 ng g\(^{-1}\). The sample from BZ had the highest concentration of PFOS, which was also higher than the reported levels of PFOS in sediments or soils for other regions of the world (Hekster and Voogt, 2003; Higgins et al., 2005; Voogt and Roon, 2005). As discussed above, PFOS in site BZ can hardly be interpreted by changes in natural environmental conditions because of the intensive human activities in this area. Concentrations of PFOS have been reported ranging between 14.4 and 2610 ng g\(^{-1}\) in domestic sludge from the USA (Higgins et al., 2005) and between 278 and 5383 ng g\(^{-1}\) in sewage sludges from sixteen cities of China (Guo et al., 2008). Comparatively, the concentrations of PFOS in sediment samples from Yangtze River Delta were at par with the values reported for domestic sludge (Guo et al., 2008; Higgins et al., 2005).

The depth profile/distribution of PFOS in the sediment was assessed using column samples from BZ. The content of PFOS decreased from 536.7, 306.1, to 138.1 ng g\(^{-1}\) with increase in the sampling depth (Fig. 2). The sampling location BZ was located in the near shore region of Chongming Island, which was the largest estuarine alluvial island in the world. Sequel to the barrier of Taiwan warm current, Yangtze River sediment settled inland in the west of 123°15’E at a general rate of 1–3 cm per year, the highest being 5 cm per year (Wei et al., 2007a,b). Given the sedimentation process, the sediment depth profile represented the increased PFOS pollution in over recent years in this region.

### 3.4. Effect of salinity on the sediment–water distribution of PFOS

The partition of organic pollutants between water and sediment was one of the most important factors affecting their environmental behavior and fate. Distribution coefficient (K\(_d\)) was the most commonly used parameter in the evaluation of organic pollutants partitioning in the water environment. K\(_d\) was calculated by the formula presented below:

\[
K_d = \frac{C_s}{C_w}
\]

where \(C_s\) and \(C_w\) were the concentrations of organic pollutant in sediment sample (ng g\(^{-1}\)) and in water sample (ng L\(^{-1}\)) respectively. Fig. 3 showed that K\(_d\) were significantly correlated to the salinity (Pearson Correlation = 1.000, n = 4). It was reported that the K\(_d\) of

![Fig. 2. Mean concentrations of PFOS in sediment samples from BZ at different sampling depth. Error bar was calculated by the equation as “Error bar = Standard Deviation/SQRT (n)”, n was the number of parallel samples, in our experiment, n = 3.](image)

![Fig. 3. Relationship between salinity and distribution coefficient (K\(_d\)) of PFOS between water and sediment.](image)

### Table 1

Summary of sample locations and sample characteristics.

<table>
<thead>
<tr>
<th>Location</th>
<th>Water</th>
<th>Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling</td>
<td>pH</td>
<td>Particle size (μm)</td>
</tr>
<tr>
<td>Site</td>
<td>sample</td>
<td>(μm)</td>
</tr>
<tr>
<td>BZ</td>
<td>8.25</td>
<td>65.89</td>
</tr>
<tr>
<td>BL</td>
<td>8.47</td>
<td>20.00</td>
</tr>
<tr>
<td>JN</td>
<td>8.12</td>
<td>7.41</td>
</tr>
<tr>
<td>JB</td>
<td>8.08</td>
<td>24.09</td>
</tr>
</tbody>
</table>

### Table 2

Concentrations of PFOS in water and sediment samples.

<table>
<thead>
<tr>
<th>Concentrations</th>
<th>Water (ng L(^{-1}))</th>
<th>Sediment (ng g(^{-1}) dry wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BZ</td>
<td>703.3 ± 43.33*</td>
<td>536.7 ± 29.78</td>
</tr>
<tr>
<td>BL</td>
<td>143.9 ± 20.15</td>
<td>72.9 ± 10.28</td>
</tr>
<tr>
<td>JN</td>
<td>363 ± 10.06</td>
<td>139.0 ± 25.71</td>
</tr>
<tr>
<td>JB</td>
<td>41.7 ± 0.56</td>
<td>196.2 ± 49.44</td>
</tr>
</tbody>
</table>

* S.D. value.
some organic pollutants positively correlated with salinity (Brunk et al., 1997; Luo et al., 2008). The authors studied the sorption of PFOS on natural sediment in previous studies, which suggested that the sorption of PFOS onto suspended sediment particles increased by a factor of 6 at pH 8.0 as the ionic strength increased from 0.005 mol L$^{-1}$ to 0.5 mol L$^{-1}$. Desorption hysteresis occurred over all the studied salinity and pH values. Consequently, PFOS could be increasingly sorbed by the suspended particles and settled into the sediment as the salinity increased (You et al., in press). Potassium salt of PFOS has a solubility of 370 mg L$^{-1}$ in freshwater and 25 mg L$^{-1}$ in filtered seawater (Development, 2002), which demonstrated a significant salting out effect.

The sink effect of estuary was directly confirmed by comparing concentrations of PFOS in the water and in the sediment at different salinity sites (Fig. 4). At low salinity area of site BL, the concentration of PFOS in water was high (143.9 ng L$^{-1}$) but relatively low in the sediment (72.9 ng g$^{-1}$). In contrast, at a higher salinity area of JB, the concentration of PFOS in water was low (41.7 ng L$^{-1}$) but relatively high in the sediment (196.2 ng g$^{-1}$). The turn-over point (i.e. the crossing point of PFOS in water and sediment) was around 1.1 $\mbox{mg L}^{-1}$ for PFOS. These results suggested that when the Yangtze River flows into the East China Sea, PFOS could be largely scavenged into the sediment in the estuary area due to the increased sorption as the salinity increases. Data of site BJ was not included in the analysis of Fig. 4, because PFOS level in site BJ was dominated by artificial pollution rather than the natural changes in salinity. This study suggested that estuaries may be an important sink for PFOS in its transport pathways in aquatic environment.

3.5. Effect of sediment characteristics on the distribution of PFOS

Correlation analysis between the sediment characteristics (TOC and sediment profile) and the calculated K_d values were also drawn to predict the effect of sediment constituents on the uptake of PFOS by the sediment. The Pearson correlations between K_d and TOC, clay, silt and sand were 0.71, 0.55, 0.49 and 0.50 respectively, which suggested that the enrichment of PFOS on the sediment was not significantly correlated to the content of TOC as well as clay, silt and sand. This result is different from the earlier findings of Higgins and Lathy (2006), but agrees to the results presented by Becker et al. (2008). The sequence of Pearson correlation suggested that the content of TOC contribute more to the sorption of PFOS than the other inorganic sediment constituents.

3.6. Environmental fate of PFOS

Estuaries are important land–ocean interaction areas with complex conditions of rapid and monumental changes. Meanwhile, estuaries are particularly susceptible to environmental abuse since industrial activities are often concentrated near them. An important consideration for water quality management is the capacity of an estuary to filter or retain contaminants (Brunk et al., 1997). The amounts of PFOS in Yangtze River Estuary were much higher than the reported values in other places of Yangtze River (So et al., 2007) and near oceans (Hekster and Voogt, 2003), and were comparable to the near oceans value reported by Wei et al. (2007a,b). The increasing value of PFOS sorbed onto sediment, the increasing irreversibility of the sorption process with increase in salinity (You et al., in press), and the high correlation between K_d and salinity, suggested that the affinity of the sediment for PFOS would be higher during salt intrusion. PFOS may be carried with the river water and transported for long distances before it reaches to the sea and largely scavenged to the sediment in the estuaries due to the dramatic change in salinity.

4. Conclusion

Study on the distribution of PFOS in water and sediment in Yangtze River Estuary showed that salinity was an important controlling parameter affecting the transport of PFOS in aquatic environment. At low salinity area (site BL near the river side), the concentration of PFOS was high in water (143.9 ng L$^{-1}$) but relatively low in the sediment (72.9 ng g$^{-1}$). In contrast, at high salinity area (site JB near the sea side), the concentration of PFOS in water was low (41.7 ng L$^{-1}$) but relatively high in the sediment (196.2 ng g$^{-1}$). As the salinity $S_m$ increased from 0.18 to 3.31, the distribution coefficient (K_d) between sediment and water linearity increased from 0.76 to 4.70 L g$^{-1}$. PFOS in the sediment column samples (site BZ) increased from 138.1, 306.1, to 536.7 ng/g as the sampling depth decreased from 34 to 50 cm, 17–34 cm, and 0–17 cm, revealing an enrichment trend of PFOS into the sediment over the recent years. The study suggests that PFOS can be largely scavenged to the sediment in estuary due to the dramatic change in salinity.

Acknowledgements

The study is supported by the National Natural Science Foundation of China [20621703] and a National Key Fundamental Study Project (2010CB933600). Chun You wishes to thank Nurudeen Abiola Oladoja for helpful discussion.

References


