Determination of perfluorinated compounds (PFCs) in solid and liquid phase river water samples in Chao Phraya River, Thailand

Chinagarn Kunacheva, Shuhei Tanaka, Shigeo Fujii, Suwanna Kitpati Boontanon, Chanatip Musirat and Thana Wongwattana

ABSTRACT

Perfluorinated compounds (PFCs), especially perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are fully fluorinated organic compounds, which have been used in many industrial applications. These chemicals have contaminated surface water all over the world even in developing countries like Thailand. The previous study showed the contamination in Chao Phraya River in 2006 and 2007. The purposes of this field study were to determine the solid and liquid phase of PFCs contamination in Chao Phraya River and to compare the changes of PFC concentration in 2008. Surveys were conducted in the lower reach of Chao Phraya River in the industrialized area. A solid phase extraction (SPE) coupled with HPLC-ESI-MS/MS were used for the analysis for ten PFCs. Ten PFCs were analyzed to identify the contamination in both solid and liquid phases. PFCs were detected in both the solid and liquid phase in every sample. PFOA was the most dominant PFC while PFPA and PFOS were also highly detected in most samples. The average loadings of PFPA, PFOA and PFOS in Chao Phraya River were 94.3, 284.6 and 93.4 g/d, respectively. PFOS concentrations did not show differences between 2006 and 2008. However, PFOA concentrations were higher in 2008/5/26, while comparing other samplings. The ratio of solid : liquid PFPA (2.1 : 1.0) [(ng/g)/(ng/L)] was lower than PFOA (13.9 : 1.0) [(ng/g)/(ng/L)] and PFOS (17.6 : 1.0) [(ng/g)/(ng/L)]. The shorter chain (more hydrophilic) PFC was better to dissolve in water rather than adsorb onto suspended solids. PFOS also showed more potential to attach in the suspended solids than PFOA.

Key words | micropollutant, perfluorinated compounds (PFCs), PFOA, PFOS, surface water, Thailand

INTRODUCTION

Perfluorinated compounds (PFCs) are one of the emerging contaminants in our environmental system. They have been noted as one of the important environmental problems in recent years due to their occurrences and properties. PFCs are the man-made surfactant, which are formed by replacing hydrogen bonds in the hydrocarbon chain by fluorine atoms. The carbon-fluorine bond is one of the strongest in nature, which makes them highly stable against extreme physical, chemical and biological conditions (Key et al. 1997; 3M 1999). These specific compounds have special oil and water resistance properties, which have been used in many applications such as surface treatment, paper protection, performance chemical, coating materials, emulsifier and surfactant (Key et al. 1997; Kissa 2001). The most commonly used PFCs are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which have been used in many kinds of products. These two chemicals have been in production (Alexander et al. 2003). Once PFOS and PFOA are released into the environment, these chemicals persist and are distributed throughout the global environment. They have been found in surface water and tap water in both developed and developing countries from around the world including North America, Europe and Asia (Berger et al. 2004; Saito et al. 2004; Sinclair et al. 2004; Sinclair & Kannan 2006).

In addition to the water environment, PFOS and PFOA have also been detected in livers, bladders and blood

samples of human and many kinds of animal including, fish, birds, and marine mammals (Renner 2001). Animals in the higher food chain such as mink and bald eagles (fish-eating animals) contained higher concentration of PFOS, representing bio-accumulative properties (Giesy & Kannan 2004). Animals in the higher food chain such as mink and bald eagles (fish-eating animals) contained higher concentration of PFOS, representing bio-accumulative properties (Giesy & Kannan 2004). Recently, due to their persistent bio-accumulation, long-range transportation and toxic effects, PFC control regulations (EC 2006; USEPA 2006) have been released. PFOS has been shown to be toxic in rats and rabbits in the laboratory (Renner 2003; 3M 2003). Recently, due to their persistent bio-accumulation, long-range transportation and toxic effects, PFC control regulations (EC 2006; USEPA 2006) have been released. PFOS has been shown to be toxic in rats and rabbits in the laboratory (Renner 2003; 3M 2003). PFOS was also categorized as a persistent organic pollutant (POP) in the 4th meeting of the conference of the parties to the Stockholm Convention in May 2009 (Earth Negotiations Bulletin 2009).

In Thailand, PFCs were detected in the Chao Phraya River (PFOS 1.9 ng/L, PFOA 4.7 ng/L) and Bangpakong River (PFOS 0.7 ng/L, PFOA 0.7 ng/L), located on the eastern area of Chao Phraya River (Kunacheva et al. 2006). Chao Phraya River passes through the urban area and receives wastewater from both industrial and domestic activities. Since many regulations have been used, there might be changes in the PFC contamination in this river. It is essential to identify the PFC contamination in the river not only in the liquid phase but also in the solid phase. The purposes of this field study were to determine the solid and liquid phase of PFC contamination in Chao Phraya River and to compare the PFC contamination of this river during 2006–2008.

**MATERIALS AND METHOD**

**Reagents and chemicals**

In this study, ten PFCs were selected as target chemicals. Standard reagents were obtained from Wellington Laboratories, Canada, with purities of >99% (Table 1). PFOS stock solution was prepared by dissolving perfluorocarboxylic acids mixed solution (PFC-MXA) and perfluorosulfonates mixed solution (PFS-MXA) into 100 mL acetonitrile (LC/MS grade) and stored in polypropylene (PP) bottles at 4°C. PFOS standard solutions were prepared by diluting different volumes of single stock solutions together into 40% acetonitrile solvent. These multi-component standards contained the same concentration of each PFC. Methanol, acetonitrile and ultrapure water were of LC/MS grade and purchased from Wako, Japan.

**Field campaign and sites**

Chao Phraya River basin is the major river system in Central Thailand, which supplies water to a major metropolitan region. It covers 160,000 km², representing 30 percent of the country’s total area and it is the source water for 23 million people (ONWRC 2005). The Chao Phraya basin is mountainous with agricultural valleys found in the upper region. The middle region contains terrestrial plains that are highly productive for agriculture. This study focused on the lower reach of Chao Phraya River (65 km to the

<table>
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<tr>
<th>Compound</th>
<th>No. of Carbon</th>
<th>Parent Ion (m/z)</th>
<th>Daughter Ion (m/z)</th>
<th>CE (eV)</th>
<th>Retention time (min)</th>
<th>LOQ (ng/L)</th>
<th>Liquid (n = 4)</th>
<th>Solid (n = 4)</th>
<th>Analytical Blank (ng/L)</th>
<th>Recovery (%)</th>
<th>Ave ± SD</th>
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<td>219</td>
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<td>0.5</td>
<td>ND</td>
<td>ND</td>
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<td>269</td>
<td>−15</td>
<td>3.2</td>
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<td>−15</td>
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<td>0.3</td>
<td>0.1</td>
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<td>82 ± 17</td>
<td>82 ± 8</td>
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<tr>
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<td>369</td>
<td>−15</td>
<td>8.1</td>
<td>0.5</td>
<td>0.2</td>
<td>0.5</td>
<td>98 ± 7</td>
<td>105 ± 9</td>
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<tr>
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<td>463</td>
<td>419</td>
<td>−15</td>
<td>10.9</td>
<td>0.4</td>
<td>0.1</td>
<td>0.1</td>
<td>106 ± 8</td>
<td>103 ± 9</td>
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<td>469</td>
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<td>13.8</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>105 ± 7</td>
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<td>−15</td>
<td>16.7</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1</td>
<td>107 ± 10</td>
<td>111 ± 6</td>
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<tr>
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<td>C12-A</td>
<td>613</td>
<td>569</td>
<td>−17</td>
<td>19.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>77 ± 15</td>
<td>61 ± 13</td>
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<td>C6-S</td>
<td>399</td>
<td>80</td>
<td>−90</td>
<td>8.9</td>
<td>0.4</td>
<td>ND</td>
<td>ND</td>
<td>105 ± 15</td>
<td>74 ± 21</td>
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<tr>
<td>PFOS</td>
<td>C8-S</td>
<td>499</td>
<td>80</td>
<td>−90</td>
<td>15</td>
<td>0.2</td>
<td>ND</td>
<td>0.1</td>
<td>112 ± 10</td>
<td>101 ± 16</td>
<td></td>
</tr>
</tbody>
</table>

Note: CE = collision energy, LOQ = limit of quantification, Ave = average, SD = standard deviation, ND = not detected. A = perfluorinated carboxylic acids (PFCAs), S = perfluoralkyl sulfonate (PFAS).
Gulf of Thailand), which flows through Bangkok city. There are dense residential, commercial and industrial areas along the side of the river through the Gulf of Thailand. The possibility of detecting PFCs in this area was highly expected especially around the industrial activities (Prevedouros et al. 2006). The sampling in Chao Phraya River was conducted on 2008/5/26 and 2008/8/4 during the rainy season in Thailand. May is the first month of the rainy season, expecting to detect higher PFC contamination due to the first flush run off. Six sampling points in Chao Phraya River mainstream (CH1–CH6) and eight points from the tributaries (CS1–CS8) were selected, as in Figure 1. The tributaries of Chao Phraya River receive wastewater from both domestic and industrial activities.

Sample collection

Samples were collected by grab-sampling using a polypropylene container. New 1.5 L narrow-neck polyethylene terephthalate (PET) bottles with screw caps were used as sampling containers. PET bottles were washed by methanol and dried prior to use. Bottles were rinsed three times by the samples before sampling. After sampling, the samples were brought back to laboratory and the pre-treatment carried out in the same day.

Solid-phase extraction

Liquid phase samples

A collected sample was filtered by 1 μm GF/B glass fiber filter to separate suspended solids. Filtrate (500 mL) was loaded into a PresepC-Agri (C18) cartridge, which was used for concentrating PFCs, at a flow rate 10 mL/min (Kunacheva et al. 2009). The cartridge was preconditioned by 10 mL of methanol (LC/MS-grade) followed by 2×10 mL of ultrapure water (LC/MS-grade) before use. The above procedures were completed in Thailand and the cartridges were brought back to Japan for further analysis. In Japan, each cartridge was dried by air for one hour, eluted by 2×2 mL LC/MS-grade methanol, evaporated to dryness with nitrogen gas, and reconstituted into 40% LC/MS-grade acetonitrile to a final volume of 2 mL. PFCs in filtrates were concentrated by a factor of 250 times. PFC standards were spiked (10 ng/L) into a duplicated sample before loading to the cartridge to find their recoveries.

Solid phase samples

The solid phase sample that was separated by GF/B filter (Filtered volume: 500 mL) was further analyzed by using Accelerated Solvent Extraction (ASE-200). The filters were air dried and inserted into ASE cells for extraction. The standard 10 ng/L was spiked into the duplicated cell before extraction. The extraction was done by using LC/MS-grade methanol as a solvent. The extraction was run for three cycles (15 min per one cycle) by using pressure 2,000 psi and temperature 100 °C. Then, the extracted sample was diluted with LC/MS-grade ultrapure water into 1 L, loaded to a PresepC-Agri (C18) cartridge and the same procedure continued with as the liquid phase samples.

HPLC-electrospray tandem mass spectrometry

Separation of PFCs was performed by using Agilent 1200SL high-performance liquid chromatography (HPLC). Extract 10 μL was injected to a 2.1×100 mm (5 μm) Agilent Eclipse XDB-C18 column. The mobile phase consisted of (A) 5 mmol/L ammonium acetate in ultrapure water (LC/MS grade) and (B) 100% acetonitrile (LC/MS-grade). At a
flow rate of 0.25 mL/min, the separation process started with an initial condition of 30% (B), increasing to 50% (B) at 16.5 min, then to 70% (B) at 16.6, holding at 70% (B) for 3.4 min, going up to 90% (B) at 21 min, staying at 90% (B) for 1 min, and then ramping down to 30% (B). The total running time was 34 min for each sample. For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS). The mass spectrometer was operated in the electrospray ionization (ESI) negative mode. Analyte ion was monitored using multiple reaction monitoring (MRM) mode. The analytical parameters of each PFC are shown in Table 1.

**Extraction QC and characterization**

The calibration curves for quantification, consisting of six points covering 0.05 to 10 µg/L, generally provided linearity with determination coefficients (R²) of more than 0.995 in every compound. Limit of detection (LOD) for HPLC/MS/MS was defined as concentration with signal to noise ratio (S/N) equal to 3:1. Practically, the limit of quantification (LOQ) was used for quantifying analyte, which was defined by S/N 10 : 1 (Saito et al. 2003), (Table 1). The duplicated analysis was also performed on all samples and coefficients of variations (CV) of concentration were below 20%. All analytical blanks (solid phase 4 samples and liquid phase 4 samples) were extracted by the same method as the samples by using ultrapure water (LC/MS-grade) to identify the contamination during the analytical procedures (Table 1). A recovery test was done for all the samples. The average recovery percentage of the solid and liquid phase of each analyte is listed in Table 1. Statistical analyses were performing using Microsoft Excel at a significance level of α = 0.05. ANOVA single factor was used for the correlations between concentrations of each sampling.

**RESULTS AND DISCUSSION**

**PFC contamination in Chao Phraya River**

Sampling was conducted in Chao Phraya River, which is located in the urban area (Bangkok City) receiving wastewater from both industrial and domestic activities. Six sampling points in Chao Phraya River mainstream (CH1-CH6) and eight points from the tributaries (CS1-CS8) were selected. Table 2 shows the statistics of PFC concentration in Chao Phraya River on 2008/5/26 and 2008/8/4. PFCs were detected in all samples along the river indicating that most of the areas were contaminated by PFCs.

On 2008/5/26, ten PFC concentrations in the tributaries averaged 24.3 and 10.9 ng/L in the liquid and solid phase, respectively. Lower levels of these PFCs were detected in the mainstream, which contained 18.5 ng/L in the liquid phase and 3.2 ng/L in the solid phase. High concentration from the tributaries indicated that there are many point sources and non-point sources in this area. The relative abundances of PFCs in Chao Phraya River are shown in Figure 2. PFOA was the most dominant PFC contributing 48%, while PFPA and PFOS were also highly detected contributing 18 and 10%, respectively. PFOA was detected at 46% (liquid) and 41% (solid) in tributaries. PFOA was also the highest detected in the main stream with 58% (liquid) and 41% (solid). Another seven PFCs accounted for less than 10% of the ten PFCs. The large portion of PFPA contaminated in this area was unique compared to Japanese rivers, in which PFHpA and PFNA were the main detected PFCs besides PFOS and PFOA (Murakami et al. 2008). PFOA and PFOS (combined liquid and solid phase) were ranged from 5.5 to 36.8 ng/L and <LOQ–14.1 ng/L. These levels of contamination were comparable to the geometric mean of PFOS and PFOA in the surface water in Japan (Saito et al. 2004). The highest concentration of both PFOS (14.1 ng/L) and PFOA (56.8 ng/L) were found at CS2, where industrial zones and a port were located in the area. The same location also detected the highest PFOS and PFOA concentration in 2006 and 2007 (Kunacheva et al. 2009). Industrial discharges, which have been reported as the major source of PFCs contaminated in surface water in many countries (Hansen et al. 2002; Sinclair & Kannan 2006; Saito et al. 2004; Yu et al. 2009), could be the source of PFC contamination.

On 2008/8/4, a lower concentration of PFCs was detected. The ten PFCs concentration in tributaries averaged 7.3 and 4.4 ng/L in the liquid and solid phase, respectively. Lower levels of these PFCs were detected in the mainstream, which contained 4.4 ng/L in the liquid phase and 2.7 ng/L in the solid phase. PFDA, PFUnA and PFDoA were detected as lower than LOQ. PFOA, PFOS and PFPA were the major PFCs for the last sampling (2008/5/26) accounting for 43, 24 and 13%, respectively, while other PFCs contributed less than 10%. Lower concentrations of PFCs were detected in this period (August), which is in the middle of the rainy season in Thailand. The higher concentration found in the first sampling in May (first month of the rainy season) could be due to the first flush run off, which is possibly one of the sources of
Table 2 | PFC concentrations in liquid and solid phases of Chao Phraya River samples on 2008/5/26 and 2008/8/4

<table>
<thead>
<tr>
<th>Date</th>
<th>Sample</th>
<th>n</th>
<th>pH</th>
<th>Temp (°C)</th>
<th>SS (mg/L)</th>
<th>Phase</th>
<th>PFCs Concentration (ng/L)</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PFPA</td>
</tr>
<tr>
<td>2008/5/26</td>
<td>Tributaries</td>
<td>8</td>
<td>7.1</td>
<td>31</td>
<td>73</td>
<td>Liquid</td>
<td>Ave 6.2</td>
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<td></td>
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<td>Solid</td>
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<td></td>
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<tr>
<td></td>
<td>Main stream</td>
<td>6</td>
<td>7.1</td>
<td>31</td>
<td>77</td>
<td>Liquid</td>
<td>Ave 2.9</td>
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<td></td>
<td>Solid</td>
<td>Ave 0.2</td>
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<td></td>
<td></td>
<td>SD 0.2</td>
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<tr>
<td>2008/8/4</td>
<td>Tributaries</td>
<td>8</td>
<td>7.0</td>
<td>30</td>
<td>52</td>
<td>Liquid</td>
<td>Ave 0.9</td>
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<td>Solid</td>
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<td>SD 0.1</td>
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<td></td>
<td>Main stream</td>
<td>6</td>
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<td>30</td>
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<td>SD 0.1</td>
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</table>

Note: n – number of sample, Ave – average, SD – standard deviation, <LOQ – less than limit of quantification, ND – not detected.
PFCs (Murakami et al. 2009), or the fluctuation of industrial usage. The most dominant PFC was PFOA, which was found with an average of 3.1 ng/L (liquid + solid). PFOS concentration in the combined phase (liquid + solid) was comparable to the last sampling (2.9 ng/L) with an average concentration of 3.8 ng/L. Despite the lower concentration detected in this sampling (2008/8/4), comparable relative abundance of PFCs with the previous sampling (2008/5/26) confirmed that PFOS, PFOA and PFPA are the major PFCs contaminating this area (Figure 2). The highest combined PFC point was CS2, similar to the first sampling, with a combined ten PFC concentration of 45.4 ng/L. This tributary was the most contaminated in this area indicating that the industrial activities could be a major source of these compounds.

Figure 3 shows a comparison of PFPA, PFOA and PFOS concentrations on 2008/5/26 with those on 2008/8/4. Most of the plots are below the 1 : 1 linear line. Ratios of PFPA, PFOA and PFOS concentrations on 2008/5/26 to those on 2008/8/4 were calculated as $4.3 : 1.0$, $4.5 : 1.0$ and $1.0 : 1.0$, respectively. This showed that PFPA and PFOA on 2008/5/26 were detected as much higher than those on 2008/8/4; in contrast, PFOS was detected at a comparable level on both samplings. Decreasing levels of PFPA and PFOA contamination might be due to the fact that the rate of those usages was diverse. Furthermore, to calculate mass loading, flow rate data were obtained from the Royal Irrigation Department, Thailand (Royal Irrigation Department (Thailand) 2008). Flow rates (monthly average) of Chao Phraya River were reported to be $30.2 \times 10^6$ m$^3$/d in 2008/5 and $24.3 \times 10^6$ m$^3$/d in 2008/8. The average loadings of PFPA, PFOA and PFOS in the two samplings were 94.3, 284.6 and 93.4 g/d, respectively. This PFOA contamination was comparable to those in the Yodo River, Japan in 2004 and 2005 (Lien et al. 2008), however, the PFOS loadings
were much higher in Chao Phraya River than those in Yodo River.

**Solid and liquid phase of PFCs**

Figure 4 shows the solid phase (ng/g) and liquid phase (ng/L) concentrations of PFPA, PFOA and PFOS in Chao Phraya River. The ratio of solid : liquid PFPA (2.1 : 1.0) [(ng/g)/(ng/L)] was lower than PFOA (13.9 : 1.0) [(ng/g)/(ng/L)] and PFOS (17.6 : 1.0) [(ng/g)/(ng/L)]. The shorter chain (more hydrophilic) PFC was better at dissolving in water than adsorbing onto suspended solids. To compare between PFOS and PFOA, PFOS had more potential to attach onto the suspended solids than PFOA (Higgins & Luthy 2006; Ahrens et al. 2010). These results show that PFC concentrations in suspended solids could not be negligible. To calculate and compare the results of PFC contamination, it is essential to analyze both solid and liquid phase samples. However, this is a preliminary result on solid and liquid phase PFC interaction. A further study should be done to understand the fate and transport of PFCs in the water environment.

**Comparison of PFOS and PFOA concentrations with 2006 and 2007**

Figure 5 shows the geometric mean and concentrations of each sample of PFOS and PFOA in the Chao Phraya River in this study compared with those in 2006 and 2007 (Kunacheva et al. 2009). PFOS and PFOA were detected during 2006 to 2008. PFOS concentration was comparable, indicating that PFOS was still used in the manufacturing and products even though the major PFC producing company began to phase out their usage of PFOS in 2000. PFOS concentration detected during 2006 and 2008 did not show differences among the samplings. PFOA concentration on 2008/5/26 was about 2 times higher than in 2006 and 2007. PFOA concentration on 2008/5/26 was also higher than those on 2008/8/4. The reason could be due to the first flush run off or fluctuating usage.

Regulation to control the production and usage of both PFOS and PFOA is needed not only in developed countries but also in developing countries. In 2009, PFOS was categorized as a persistent organic pollutant (POP) (Earth Negotiations Bulletin 2009). Decreases of PFOS contamination in surface water will be expected in years to come. It is essential to continue to monitor PFOS and PFOA concentration in the future.

**CONCLUSIONS**

The survey was conducted in the industrialized area in Chao Phraya River, Thailand. Ten PFCs were analyzed to identify the contamination in both solid and liquid phases. PFCs were detected in both the solid and liquid phase in every sample. PFOA was the most dominant PFC, while PFPA and PFOS were also highly detected in most samples. The
average loadings of PFPA, PFOA and PFOS in Chao Phraya River were 94.3, 284.6 and 93.4 g/d, respectively. PFOS concentrations did not show differences between 2006 and 2008. However, PFOA concentrations were higher in 2008/5/26, compared to other samplings. The reason could be due to the first flush run off or fluctuating usage. The ratio of solid : liquid PFPA (2.1 : 1.0) [(ng/g)/(ng/L)] was lower than PFOA (13.9 : 1.0) [(ng/g)/(ng/L)] and PFOS (17.6 : 1.0) [(ng/g)/(ng/L)]. The shorter chain (more hydrophilic) PFC was better to dissolve in water rather than adsorb onto suspended solids. PFOS also showed more potential to attach to suspended solids than PFOA. To calculate and compare the results of PFC contamination, it is essential to analyze both solid and liquid phase samples. The solid : liquid concentration ratio is also important for understanding the fate and transport of these compounds in the environment.

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