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PERFLUOROOCTANE SULFONATE (PFOS) AND PERFLUOROOCTANOATE (PFOA) CONTAMINATION OF WATER ENVIRONMENT IN ASIAN COUNTRIES

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ABSTRACT

PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoate), which are two emerging concerned pollutants, have been detected in environmental water of developed countries, but their observation in other parts of the world, particularly in developing countries, has not been reported. In this study, international water sampling surveys were conducted in six Asian countries with the cooperation of local universities. Their aqueous concentrations were analyzed by solid phase extraction (SPE) coupled with LC/MS measurement. Majority of surface tap water samples were contaminated with them at concentrations above the *LOQs*. Medians of PFOS concentrations (ng/L) in surface water were: Johor Bahru (7.3), Singapore (4.7), Yodo River (3.4), Shenzhen (2.5), Chao Phraya River (1.5), Kinki (1.4), Phong River (0.16), Kota Kinabalu (0.12), and Hanoi (0.08). Those for PFOA were: Yodo River (34.4); Singapore (16.4), Shenzhen (14.3), Johor Bahru (12.9), Kinki (3.3), Chao Phraya River (4.2), Hanoi (0.91), Phong River (0.66), and Kota Kinabalu (0.19). This showed high contaminated in industrialized and urbanized areas. Tap water concentrations in these areas were also contaminated at similar concentrations in their environmental water.

KEYWORDS

PFOS, PFOA, Asian countries, surface water, tap water

INTRODUCTION

Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), are man-made surfactants having wide ranges of industrial and commercial applications for several decades. In 2002, production of PFOS was phased out by a major Company (3M, 2000) due to its environmental concern. PFOS is bio-accumulative (Martine *et al.*, 2004, Taniyasu *et al.*, 2003) and considered as a new kind of POPs (UNEP, 2006). PFOS and PFOA are found as predominant perfluorinated compounds in human blood (Taniyasu *et al.*, 2003, Olsen *et al.*, 2003, Kannan, *et al.*, 2004, Kärman, *et al.*, 2004). In water environment, detection of PFOS and PFOA has been reported in USA (Hansen *et al.*, 2002, Sinclair *et al.*, 2004, 2006, Kannan, *et al.*, 2004), Nordic Europe (Berger

et al., 2004) and Japan (Taniyasu *et al.*, 2003, Saito *et al.*, 2004, Lien *et al.*, 2007). However, their appearance levels have rarely been reported in other countries. Distribution and behavior of PFOS and PFOA are not well understood and give a big room for research. This study aims to determine PFOS and PFOA concentrations in water environment in Asian countries. With focus on new places where no examination has been conducted, and two types of waters, surface water and tap water, the study would provide data for understanding the distribution and behavior of PFOS and PFOA in Asian water environment.

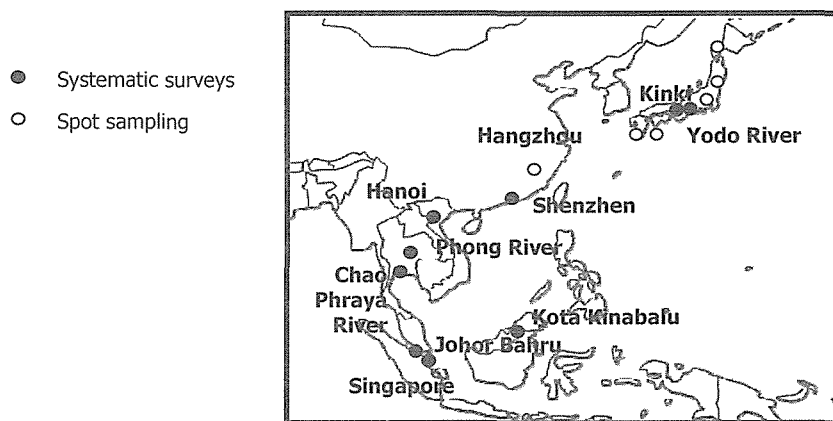


Fig. 1 Sampling locations

METHODS

Sampling areas. Sampling surveys were conducted from Nov. 2004 and Dec. 2006 in one or two areas of six Asian countries including Japan, China, Vietnam, Thailand, Malaysia, and Singapore (Fig. 1). They are Yodo River, Kinki (Japan), Shenzhen, Hangzhou (China), Hanoi (Vietnam), Phong River, Chao Phraya River (Thailand), Johor Bahru, Kota Kinabalu (Malaysia), and Singapore. The surveys were conducted basically within urban areas and their surrounding, except for Phong River basin which is characterized as an agricultural area.

Sampling campaign. Samples were collected from tap water and various types of environmental water, such as rivers, lakes, ponds, reservoirs, and others. Basically, most of surveys were systematically conducted with the help of universities there, so that several tens of samples were collected from both environmental water and tap water within a few days. A plastic or stainless steel bucket was used for sample collection, and samples were stored in disposable PET bottles at 5°C before analysis. Samples were pre-treated in sampling countries and kept in loaded SPE (solid phase extraction) cartridges during transportation to Japan for further analysis. Pre-treatment equipments and materials were consistently prepared from Japan while Milli-Q water and methanol were obtained from universities in the countries. In addition, spot sampling were also conducted, in which a few samples were brought to Japan without any pre-treatment within a couple of days.

Analysis method. Analysis procedure consisted of solid phase extraction (SPE) and liquid chromatography tandem mass spectrometry (LC-MS), which was described in our previous publications (Lien *et al.*, 2006, 2007, Tanaka *et al.*, 2006). A collected sample was firstly filtered through a glass fiber filter and about 1000 mL of the pre-filtered sample was loaded on a Presep-C Agri cartridge (Wako, Japan) using the Sep-Pak concentration system (Waters, Japan) at a flowrate of 10 mL/min. The cartridge was then eluted with 3 mL methanol and the collected solvent was dried under N₂ gas flow. Finally the sample was reconstituted with a volume of 0.5 mL methanol solvent for LC-MS quantification. HPLC instrument was Ultra Microprotein Analyzer with

column Agilent Zorbax C-18 and MS. The sample was chromatographed using a gradient flow, and the chromatographed flow was interfaced with MS system TSQ 7000 (ThermoQuest, USA), in which selected ion monitoring was applied at $m/z = 499$ for PFOS anion ($C_8F_{17}SO_3^-$) and $m/z = 413$ for PFOA anion ($C_7F_{15}CO_2^-$). PFOS peak appeared at 6.0 min, preceded by two small peaks. PFOA was detected at 2.8 min.

Method validation. PFOA (98% purity) and potassium salt of PFOS (95% purity) (Wako, Japan) were used to prepare standard solutions. Calibration curves in HPLC solvent proved the linearity of PFOS (PFOA) in a range from 0.1 $\mu\text{g/L}$ (0.2 $\mu\text{g/L}$) to 100 $\mu\text{g/L}$ with determination coefficients $R^2 > 0.997$. The limits of quantification (LOQ) which was set as coefficient of variation less than 20% were 0.05, 0.1 ng/L , respectively for PFOS and PFOA in 1000 times concentration by SPE.

Spike experiments. In the experiments, known amounts of PFOS and PFOA were spiked to original samples before SPE step, and the quantification results was compared in original samples and their spiked samples. The experiments were performed for both *Milli-Q* water samples and field samples. In both analytes, the linearity on spiking concentrations was proven in the concentration range of 0.5-100 ng/L by good determination coefficients ($R^2 > 0.99$). Extraction recoveries of *Milli-Q* water were 97% and 105% for PFOS and PFOA respectively, while those of field samples were 87% for PFOS and 95% for PFOA (in average).

Statistical treatment. In case of samples that did not have quantitative concentrations (less than LOQ), their concentrations were assumed as half of LOQ values to handle such non-numerical data in statistical calculations as well as for graph display. For the comparison of two data groups, *t-test* was used to statistically confirm the differences in their averages.

RESULTS AND DISCUSSIONS

Concentration in Surface Water

PFOS and PFOA were detected in the majority of collected samples with concentration levels higher than LOQ (PFOS 91% and PFOA 88%). Distribution of PFOS and PFOA concentrations are shown and compared in **Fig. 2**. Median of PFOS concentrations in each area was fluctuated from 0.08 ng/L in Hanoi to 7.1 ng/L in Johor Bahru, while maximum concentration was fluctuated from 0.61 ng/L in Phong River to 67.4 ng/L in Yodo River. Based on medians of PFOS concentrations sampling areas were ranked from highest to lowest as follows: Johor Bahru (7.1 ng/L , $N=6$), Singapore (4.7 ng/L , $N=24$), Yodo River (3.5 ng/L , $N=34$), Shenzhen (2.5 ng/L , $N=9$), Chao Phraya River (1.6 ng/L , $N=15$), Kinki (1.5 ng/L , $N=15$), Phong River (0.2 ng/L , $N=29$), Kota Kinabalu (0.1 ng/L , $N=21$), and Hanoi (0.1 ng/L , $N=12$).

Median of PFOA concentrations fluctuated from 0.19 ng/L to 34.4 ng/L , while maximum concentration fluctuated from 3.2 ng/L to 21,600 ng/L . The range of PFOA concentrations were higher than that of PFOS. Based on medians of PFOA concentration, sampling areas were ranked from highest to lowest as follows: Yodo River (34.4 ng/L), Singapore (16.4 ng/L), Shenzhen (14.3 ng/L), Johor Bahru (12.9 ng/L), Kinki (3.3 ng/L), Chao Phraya River (4.2 ng/L), Hanoi (0.9 ng/L), Phong River (0.7 ng/L), Kota Kinabalu (0.2 ng/L).

Spatial variation of concentration levels. As shown in **Fig. 2**, concentrations of PFOS and PFOA were relatively high in Yodo River, Singapore, Shenzhen and Johor Bahru. The median concentrations ranged in 2.5-7.1 ng/L for PFOS and in 12.9-34.4 ng/L for PFOA, which were higher than those in the other areas which ranged in 0.08-1.5 ng/L PFOS and 0.1-4.2 ng/L PFOA.

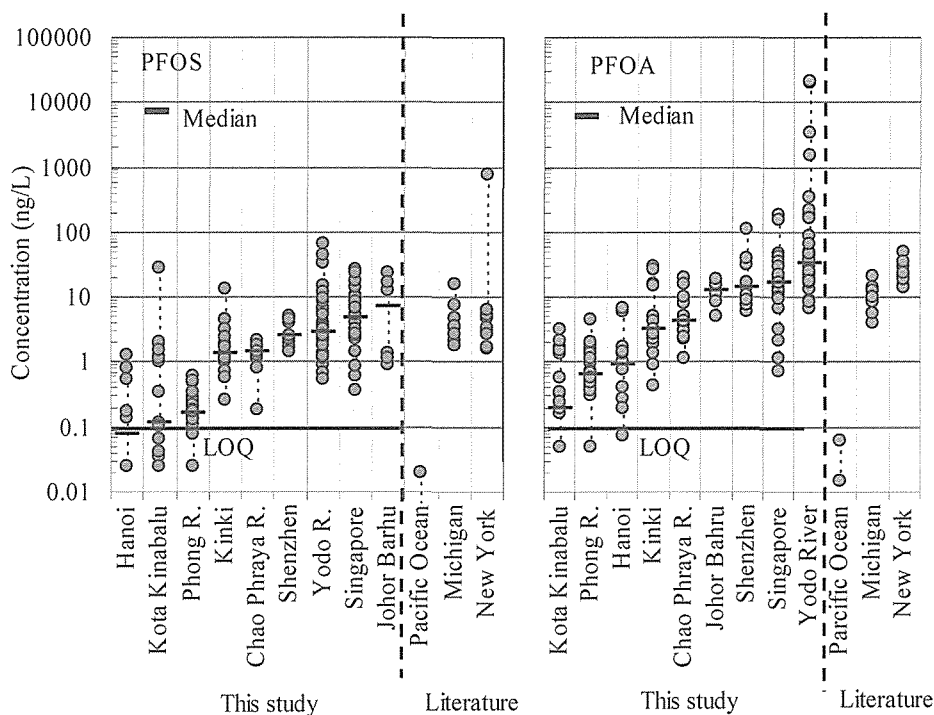


Fig. 2 PFOS and PFOA concentration in surface water

They are highly industrialized urban areas, so that industrialization and urbanization may one of the characteristics of PFOS and PFOA contamination.

Differences of concentrations were found even within a country. In Japan, the concentrations were very high in Yodo River in comparison with other rivers in Kinki region with $p < 0.05$ for PFOS and $p < 0.1$ for PFOA (t -test). Extraordinarily high PFOA concentrations of several ten thousand ng/L (several ten $\mu\text{g/L}$) were repeatedly detected in Yodo River system, but all these data were limited in Ai River catchments where a fluorochemicals factory is located. This concentration levels came to be the highest reported concentration levels of PFOA in environment reported so far. The data were also in correspondence with those reported by other researchers (Saito *et al.*, 2004, Morikawa *et al.*, 2006).

In Thailand, the concentrations in Chao Phraya River were obviously different from those in Phong River, showing p values of t -test less than 0.002 in both of PFOS and PFOA. In Malaysia, PFOA concentrations were significantly higher in Johor Bahru than those in Kota Kinabalu with $p < 0.003$. Relatively lower contamination in Phong River (an agricultural area) and Kota Kinabalu (a natural conservative area) should be due to their natural and agricultural characteristics.

Figure 2 also displays several data in literatures. Median concentration reported in USA (Sinclair *et al.*, 2004, 2006) were ranging 1.8-16.1 ng/L of PFOS and <8-21.64 ng/L of PFOA in Michigan, and 1.7-5.5 ng/L of PFOS (without 756 ng/L) and 15-21 ng/L of PFOA in New York. Therefore, concentrations found in Yodo River, Singapore, Johor Bahru and Shenzhen were comparable to those reported values. On the other hand, all of the surface water samples in this study were higher than those in Central to Eastern Pacific Ocean (Yamashita *et al.*, 2005), which were reported to be in several to several tens pg/L and were considered as the background levels. The results, therefore, implies the affect of human activities appears on contamination of PFOS and PFOA in all studied areas.

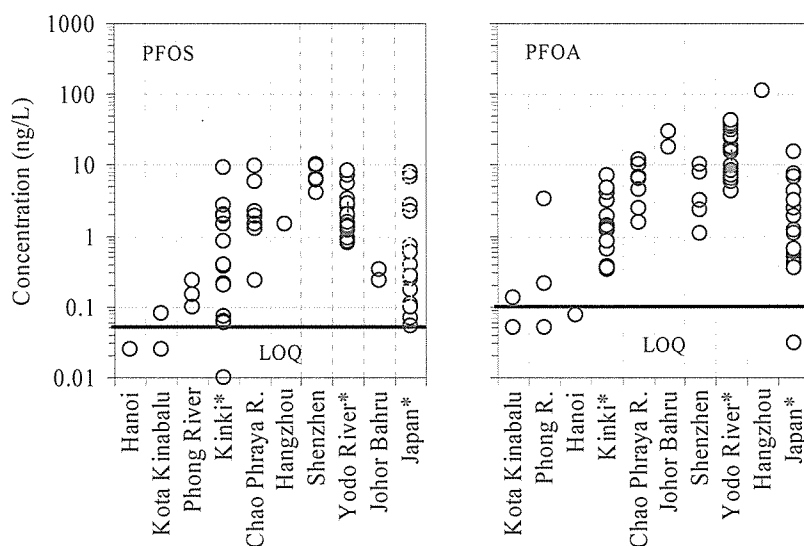


Fig. 3 PFOS and PFOA concentration in tap water (Kinki* means Kinki area excluding Yodo River, and Japan* means Japan area excluding Kinki area)

Concentrations in Tap Water

Figure 3 shows concentrations in tap water samples. PFOS and PFOA were also detected in most of tap water samples. Median (range) of PFOS concentrations in ng/L were 2.65 (0.9-8.4), 0.48 (0.01-9.13), and 0.50, respectively in Yodo River ($N=15$), other areas of Japan ($N=30$) and outside Japan ($N=37$). Those for PFOA were 11.8 (6.4-42.4), 1.4 (0.03-15.1), and 1.1 (0.05-109.3). Tap water concentrations were relatively high in samples collected in Japan including those from Kinki area and Yodo River basin. In the other countries, high concentrations were detected in Shenzhen, Hangzhou (China), Chao Phraya River (Thailand) and Johor Bahru (Malaysia).

Geometric means were considered as representative values in each area, and those of tap water and surface water were plotted in scattering graphs, as shown in **Fig 4**. The figure depicts increasing trends of tap water concentrations following increasing surface water concentrations. Linear relationships were found in legalistic charts with corresponding R of 0.47 (PFOS) and 0.84 (PFOA).

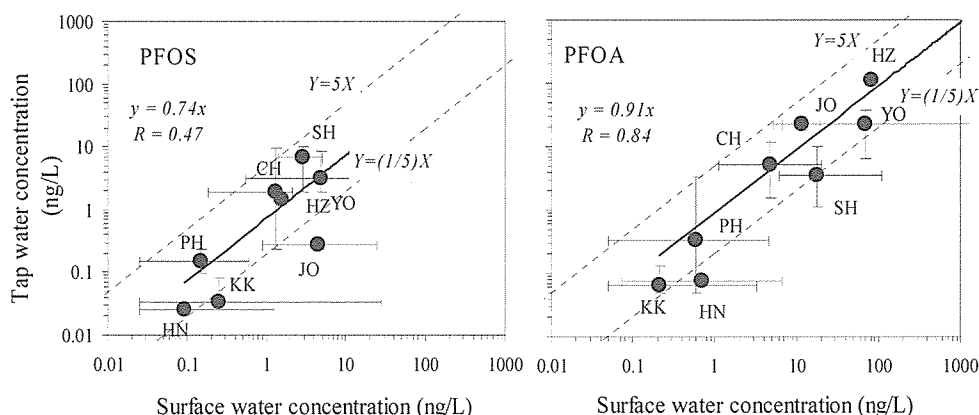


Fig. 4 Concentrations in tap water versus in surface water (YO: Yodo River, SH: Shenzhen, HN: Hanoi, PH: Phong River, CH: Chao Phraya River, JO: Johor Bahru, KK: Kota Kinabalu)

High levels of tap water concentrations were observed in Hangzhou, Yodo River, Johor Bahru, Shenzhen, and Chao Phraya River for both PFOS and PFOA, those seems to be similar to concentration levels found in surface water there. Low tap water contamination in Hanoi, Kota Kinabalu, and Phong River seem to be related to the observed concentration in the surface waters. Although, the surrounding surface water of an area might not always be tap water source, the main observation suggested that the contamination levels in tap were similar to those in surface water.

CONCLUSIONS

PFOS and PFOA concentrations of surface water and tap water were investigated at various areas in Asian countries. The main results obtained in the study are as follows:

- (1) Majority of surface water and tap water samples were contaminated with PFOS and PFOA at concentrations above LOQ.
- (2) Median of concentrations (ng/L) of surface water in each area were 7.3 (Johor Bahru), 4.7 (Singapore), 3.4 (Yodo River), 2.5 (Shenzhen), 1.4 (Kinki), 1.5 (Chao Phraya River), 0.16 (Phong River), 0.12 (Kota Kinabalu), 0.8 (Hanoi).
- (3) Those for PFOA were: 34.4 (Yodo River), 16.4 (Singapore), 14.3 (Shenzhen), 12.9 (Johor Bahru), 3.3 (Kinki), 4.2 (Chao Phraya River), 0.91 (Hanoi), 0.66 (Phong River), 0.19 (Kota Kinabalu).
- (4) Water in industrialized and urbanized areas were generally more contaminated.
- (5) Tap water was generally contaminated in PFOS and PFOA at the similar concentrations levels found in their environmental water.

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