A SIMPLE PRE-TREATMENT PROCEDURE IN PFOS AND PFOA WATER ANALYSIS AND ITS' APPLICATION IN SEVERAL COUNTRIES

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Introduction

Perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA) and their salts are fully fluorinated organic compounds and have applications in many industrial processes as well as consumer products since 50 years. Emissions in connection with the production sites are not completely understood. There has been production in the USA, Europe, Asia and Japan, and their consumption and application sites are innumerable all over the world. Therefore, field surveys to know their contamination are quite important not only in main producer countries but in any of the countries. However, it may be difficult in some countries to measure their concentration level because of their complicated analysis methods. The objectives of this study are to propose a simple pre-treatment procedure in PFOS and PFOA measurement and to compare their concentrations of surface water and tap water in Japan and the other countries.

Materials and Methods

Figure 1 shows a procedure of sample collection and pre-treatment. In PFOS and PFOA analysis, the use of TEFLON and glass materials was minimized in the whole procedure of sampling, storage, pre-treatment and measurement to avoid possible contamination or adsorption[1]. PET or PP bottles, which had been rinsed throughout with methanol and *Mili-Q* water, were used for sampling. Solid phase extraction by peristaltic pump was used as pre-treatment method abroad. When there were facilities near sampling area, the pre-treatment was carried out by using their filtration system and our loading system in these laboratories. In case of no facilities, both systems of filtration and loading were provided by ourselves. In case of no space and time available, a few tap water samples were collected in PET bottles purchased locally as bottled water. The PET bottles were rinsed well with the sampling water before filled and transported to the laboratory in Japan for further processing.

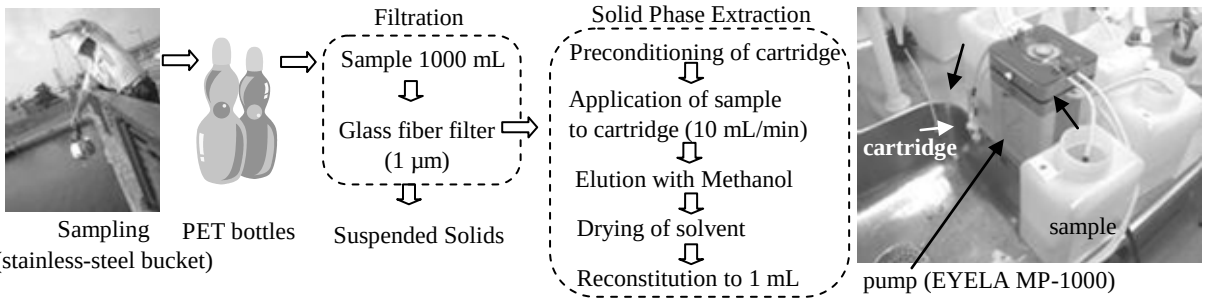

Fig. 1 A simple procedure of sample collection and pre-treatment

A sample (about 1 L) was filtered with a glass fiber filter, and was loaded at a flow rate of 10 mL/min right onto a cartridge (*Presep-C Agri*, Wako, Japan), which was conditioned with methanol followed by *Mili-Q* water rinsing right before the loading. The cartridge was then eluted with methanol. Finally, exact 1 ml of extract was collected for HPLC measurement. A 20 µl sample of each extract was applied to an Agilent Zorbax XDB C-18 column at a flow rate of 0.1 mL/min. The mobile phase consisted of 10 mM ammonium acetate and acetonitrile. The HPLC system was interfaced to TSQ 7000 (ThermoQuest, USA), atmospheric pressure ionization tandem mass spectrometer, operating in the electrospray negative mode. **Figure 2** shows a chromatographic identification of PFOS and PFOA. Quantification was based on selected ion monitoring mode detecting single product ions: $C_8F_{17}SO_3^-$ (m/z 499) for PFOS and $C_7F_{15}CO_2^-$ (m/z 413) for PFOA.

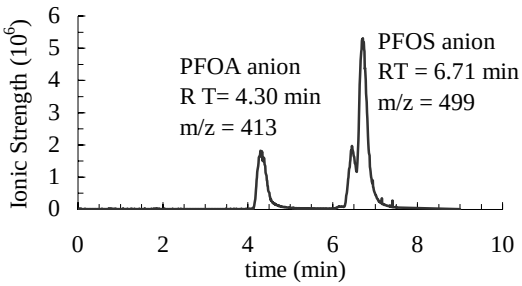

Fig. 2 Mass chromatograph of 100 µg/L PFOS and PFOA standard solution

Figure 3 shows sampling sites in this study. Sampling of environmental waters was carried out in Japan, Malaysia, Thailand, Sweden, Canada and Vietnam. Tap water was sampled in China and Singapore in addition to these countries. **Table 1** indicates sampling sites, dates and the number of samples collected. 223 samples were collected from November 2004 to March 2006. **Figure 4** shows detail sampling sites distribution in Japan. Water sampling was carried out three times in the Yodo River basin (upstream rivers of Katsura, Uji and Kizu River, downstream of Yodo River) and Ai River. 33 samples were collected in the river, while 10 samples were obtained in effluents of WWTP. Almost no rain was observed during 5 days before the sampling days.

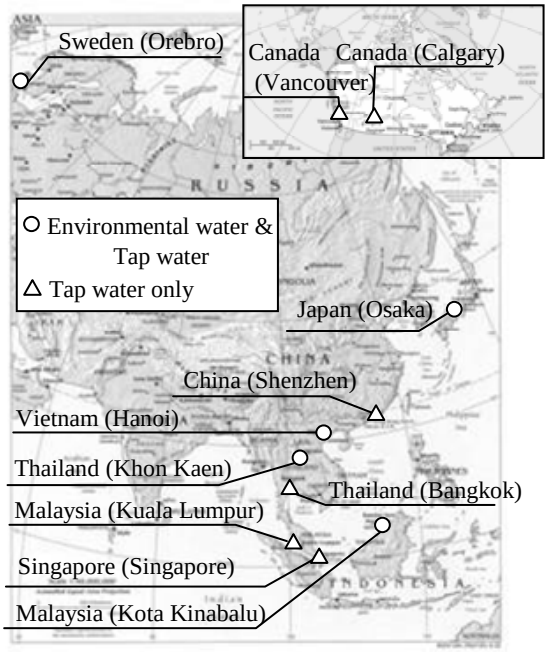

Fig. 3 PFOS and PFOA sampling sites in this study

Table 1 Sampling dates and the number of samples collected in Japan and the other countries

	City	Sampling Date	River	Lake, Pond, Wetland	WWTP	Tap or bottled water	Others	Total
Japan	Osaka etc.*	Nov.-2004, Mar.,Nov.-2005	71	-	23	12	2	108
Malaysia	Kota Kinabalu, Kuala Lunpur	Sep.,Nov.-2005	16	10	-	7	6	39
Thailand	Khon Kaen, Bangkok	Jul.-2005	28	-	-	5	1	34
Sweden	Orebro	Mar.-2006	6	5	4	3	2	20
Vietnam	Hanoi	Jan.-2006	6	4	2	3	1	16
Canada	Calgary, Vancouver	Sep.-2005	-	1	-	2	-	3
China	Shenzhen	Oct.-2005	-	-	-	2	-	2
Singapore	Singapore	Jul.-2005	-	-	-	1	-	1
Total			127	20	29	35	12	223

* Sapporo, Shiga, Kyoto, Osaka, Nara, Hyogo, Okayama and Kagawa

Results and Discussion

The limit of detection, which was given as the signal to noise ratio larger than 3, was 0.05 ng/L for PFOS and 0.1 ng/L for PFOA. Original standard curves had good linearity in the range of 0.5-100 ng/L (R^2 >0.998). Extraction standard curves also showed excellent linearity (R^2 >0.999). **Table 2** indicates extraction recoveries. Extraction efficiencies were within 10 % of the expected values for all spikeing concentrations with one exception of PFOS at 1 ng/L.

Table 3 indicates the PFOS average concentration of surface waters in rivers, lakes, WWTPs, tap waters and bottled waters. A high PFOS concentration (24.1 ng/L) was detected in effluents of WWTP, Japan. The average concentration of rivers in Japan was higher than those in the other countries. In case of tap waters, 9.5 ng/L was detected from Bangkok sample (n=1) in Thailand, however it was less than 0.3 ng/L in Khon Kaen (n=4). PFOS concentration was high in Shenzhen (China) (6.3 ng/L) and in Kagawa (Japan) (6.8 ng/L). **Table 4** indicates the PFOA average concentration. A high PFOA concentration (9,579 ng/L) was detected in Ai River, Japan. Also average concentration of a WWTP (w10) effluent in Ai River basin was significantly high (8,007 ng/L).

Figure 5 shows PFOS and PFOA concentration of surface waters in the Yodo River and Ai River basin compared with samples from other countries. PFOS and PFOA were detected throughout the survey area in the range from 0.4 to 111 ng PFOS /L and from 4 to 710 ng PFOA /L in Yodo River. The highest PFOA concentration (more than 36,000 ng/L) was detected in Ai River. **Figure 6** shows PFOA mass of surface water in Ai River. In Ai River, PFOA concentration increased significantly in front of a WWTP (w10). A mass calculation suggested that more than 1,400 g/day PFOA was present in the discharged water in Nov. 1, 2005. About 6.5 times loadings compared with Yodo River basin were discharged at Ai River basin, which has about 2 % catchment area compared with Yodo River basin (Catchment area; 163 km^2 (Ai River),

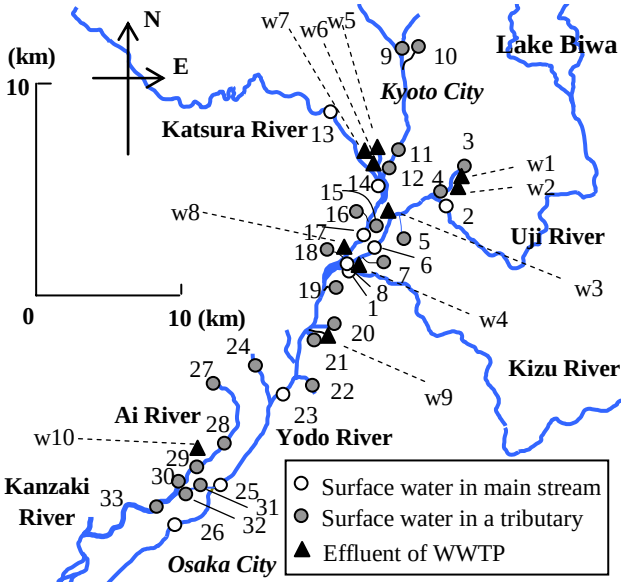

Fig. 4 Sampling sites distribution in Yodo river basin

Table 2 Extraction Recoveries

Concentration	(ng/L)	1	10	50	100
Recovery (%)	PFOS	78	109	106	96
	PFOA	109	108	99	102

Table 3 The average concentration of PFOS

PFOS (ng/L)	River	Lake, Pond, Wetland	WWTP	Tap water	Bottled water
Japan	8.3	-	24.1	1.4	-
Malaysia	5.7	0.7	-	0.1	N.D.
Thailand	0.5	-	-	2.5	0.1
Sweden	1.3	1.1	2.4	0.4	-
Vietnam	0.5	0.2	N.D.	N.D.	N.D.
Canada	-	0.1	-	N.D.	-
China	-	-	-	6.3	-
Singapore	-	-	-	0.7	-

Table 4 The average concentration of PFOA

PFOA (ng/L)		River	Lake, Pond, Wetland	WWTP	Tap water	Bottled water
Japan	Osaka, Kyoto	76	-	236	7	-
	Ai River	9,579	-	8,007	-	-
Malaysia		0.6	1	-	0.1	N.D.
Thailand		18	-	-	1	0.4
Sweden		2	0.9	2	1	-
Vietnam		3	7	0.8	N.D.	N.D.
Canada		-	0.8	-	0.2	-
China		-	-	-	3	-
Singapore		-	-	-	2	-

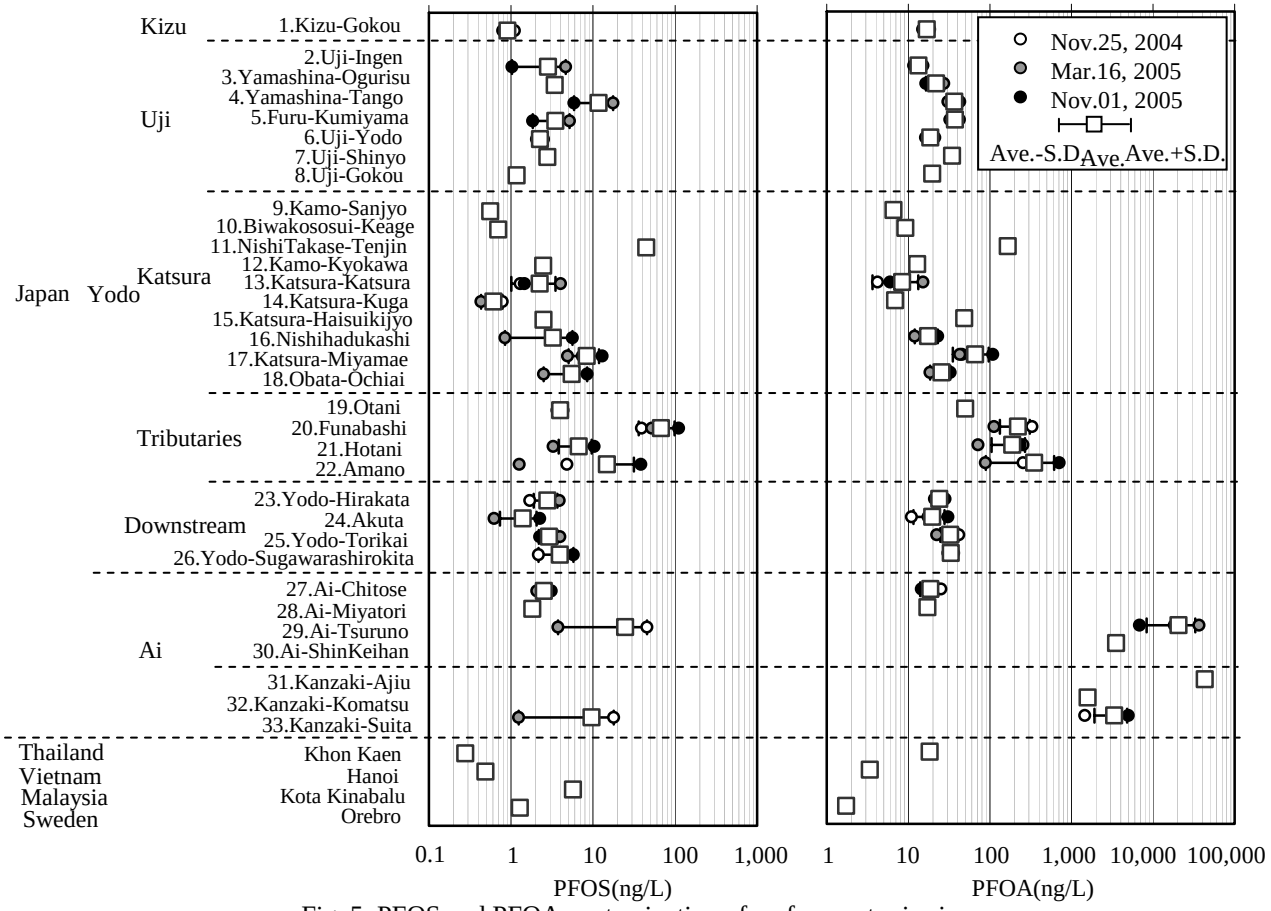

Fig. 5 PFOS and PFOA contamination of surface water in rivers

8,240 km^2 (Yodo River)). In the previous surveys, more than 4,700 g/day and 9,100 g/day PFOA were detected in front of the WWTP. There is a factory that often produces fully fluorinated organic compounds near this WWTP. More than 43,000 ng/L PFOA was detected in Ajiu-channel in Kanzaki River near this factory. A huge amount of PFOA might be discharged from this factory. As a further study, more detail surveys will be required in Ai River.

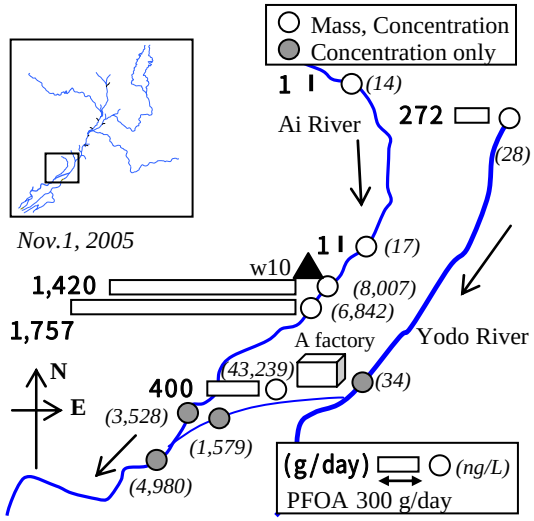

Fig. 6 PFOA mass of surface water in Ai River

Acknowledgements

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Reference

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