CONTAMINATION OF PERFLUORINATED COMPOUNDS IN WATER ENVIRONMENT OF ASIAN COUNTRIES

<u>S. Tanaka</u>¹, S. Fujii², N.P.H.Lien³, M. Nozoe¹, K. Chinagarn¹, K. Kimura¹, B. Shivakoti¹, A. Anton⁴, M. Maketab⁵, W. Wirojanagud⁶, J.Y. Hu⁷, S. Kitpati⁸, J. Shimizu⁹, S. Tittlemier¹⁰, G. Lindstrom¹¹, and N. Saito¹²

¹Research Center for Environmental Quality Management, Department of Engineering, Kyoto Univ., 1-2 Yumihama, Otsu, Shiga, 520-0811, Japan; ²Graduate School of Global Environmental Studies, Kyoto University, Yoshidahonmachi, Sakyo-Ku, Kyoto, 606-8501, Japan; ³Department of Environmental Engineering, Hanoi University of Technology, Hanoi, Vietnam; ⁴Biotechnology Research Institute, School of Science and Technology, Universiti Malaysia Sabah, Kota Kinabalu, Sabah, Malaysia; ⁵Department of Chemical Engineering, Universiti Teknologi Malaysia, Johor, Malaysia; ⁶Research Center for Environmental and Hazardous Substance Management, Khon Kaen Univ., Khon Kaen, 40002, Thailand; ⁷Department of Civil Engineering, National University of Singapore, 119260, Singapore; ⁸Department of Civil Engineering, Mahidol Univ., Salaya, Thailand; ⁹Hydrographic and Oceanographic Department, Chuo-ku, Tokyo, 104-0045, Japan; ¹⁰Food Research Division 2203D, Health Canada, Ottawa, Ontario, Canada; ¹¹MTM Research Center, Department of Natural Sciences, SE-70182, Orebro, Sweden; ¹²Research Institute for Environmental Sciences and Public Health of Iwate Prefecture, Morioka, Iwate, 020-0852, Japan

Abstract

This paper focuses on perfluorinated compounds (PFCs) including sulfonate perfluorooctane (PFOS) and perfluorooctanoate (PFOA) in water environment of seven Asian countries (Japan, Singapore, Thailand, Malaysia, China, Vietnam, and Taiwan). Some contamination levels were compared with those in Sweden, Turkey, and Canada. 1,150 samples were collected in water environment (river, lake, wetland, reservoir, wastewater treatment plant, tap water, sea water, and so on) from Nov. 2004 to Dec. 2007. Main conclusions obtained in this 1) Average are as follows: study concentration of PFOS in surface water of rivers was less than 1.0 ng/L in Hanoi, Kunming, Shimane, Khon Kaen, Canada, and Shiga. It was more than 10.0 ng/L in Osaka. 2) Average concentration of PFOS in tap water was less than 0.35 ng/L in Hanoi, Kunming, Kota Kinabalum, Khon Kaen, Johor Bahru, and Shimane. It was more than 10.0 ng/L in Bangkok and Taipei. 3)



Fig. 1 PFCs sampling sites in this study

Average concentration of PFOA in surface water of rivers was less than 1.0 ng/L in Canada, Kota Kinabalu, Orebro, and Taipei. It was significantly high in Osaka, and it was more than 15 ng/L in Kyoto, Shenzhen, Khon Kaen, and Singapore. 4) Average concentration of PFOA in tap water was less than 0.20 ng/L in Kunming, Hanoi, Taipei, Kota Kinabalu, and Canada. It was more than 10 ng/L in Osaka and Okayama in Japan.

Introduction

Perfluorinated compounds (PFCs) 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 developing countries to measure their concentration level because of their complicated analysis methods. Main objective of this study is to show contamination levels of PFCs in Asian countries by using a simple pretreatment procedure in PFOS and PFOA measurement (2006, S.Tanaka *et. al*¹).

Materials and Methods

Figure 1 shows sampling sites in this study. Sampling of environmental waters and tap water was carried out in Japan (Shiga, Kyoto, Osaka, Hyogo, Okayama, Hiroshima, Yamaguchi, Shimane, and the other cities), Singapore, Thailand (Bangkok and Khon Kaen), Malaysia (Kuala Lumpur, Johor Bahru, and Kota Kinabalu), China (Shenzhen

and Kunming), Vietnam (Hanoi), Taiwan (Taipei), Sweden (Orebro), Canada, and Turkey. Table 1 indicates sampling sites and the number of samples collected. 1,150 samples were collected from November 2004 to December 2007. In this study, 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 adsorption². PET or PP bottles, which had been rinsed throughout with methanol and Milli-Q water, were used for sampling. Solid phase extraction by peristaltic pump was used as pre-treatment method abroad. The PET bottles were rinsed well with the sampling water before filled and transported to the laboratory in Japan for further processing.

A sample (about 1 L) was filtered

Table 1 Th	e number	of sample	s collected	in 1	0 countries
------------	----------	-----------	-------------	------	-------------

Nation	Province	River	Lake, Reser voir	Sea water	WW TP	Indus trial WW	Tap water	Milli -Q	Other s	Total
Japan	Shiga	17	13	0	92	0	10	3	0	135
	Kyoto	79	0	0	97	0	7	0	0	183
	Osaka	102	0	3	57	0	26	0	0	188
	Hyogo	5	6	0	0	0	7	0	0	18
	Okayama	9	0	0	0	0	5	0	0	14
	Hiroshima	7	0	0	0	0	6	0	0	13
	Yamaguchi	3	1	0	0	0	7	0	0	11
	Shimane	2	2	0	0	0	5	0	0	9
	Others	4	0	12	0	0	18	0	4	38
Singapore		42	13	12	85	0	21	6	1	180
Thailand	Bangkok	51	2	0	0	51	11	6	0	121
	Khon Kaen	28	0	0	0	0	5	1	2	36
Malaysia	Kuala Lumpur	13	0	0	0	0	4	2	0	19
	Johorbalu	34	0	0	0	0	7	2	0	43
	KotaKinabalu	16	10	0	0	0	5	2	5	38
China -	Shenzhen	8	0	1	2	0	4	1	0	16
	Kunming	5	3	0	0	0	3	1	0	12
Vietnam	Hanoi	6	4	0	4	0	2	0	0	16
Taiwan	Taipei	5	0	2	0	0	2	1	0	10
Sweden	Orebro	6	5	0	4	0	3	1	1	20
Canada		6	3	0	0	0	10	0	0	19
Turkey		2	2	0	1	0	5	1	0	11
Total		450	64	30	342	51	173	27	13	1150

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 *Milli-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 10 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) and Agilent G6410(tripleQ), atmospheric pressure ionization tandem mass spectrometer, operating in the electrospray negative mode. In this proceeding, concentrations in dissolved matter are reported.

Results and Discussion

Figure 2 shows PFOS and PFOA concentrations in surface water of rivers in 21 cities, 10 countries. PFOS was detected throughout the survey area in the range from 0.01 ng/L to 113.3 ng/L. Average concentration of PFOS in surface water of rivers was less than 1.0 ng/L in Hanoi, Kunming, Shimane, Khon Kaen, Canada, and Shiga. It was more than 10.0 ng/L in Osaka. PFOS tends to be low in the no industrial area. PFOA was detected throughout the survey area in the range from 0.01 ng/L. 43,200 ng/L. 43,200 PFOA ng/L was detected at Ajio-channel near Kanzaki river in Nov. 2005. In Dec. 2007, 18,700 PFOA ng/L was still detected. A huge amount of PFOA might be discharged from this factory continuously. In case of PFOA, average concentration was less than 1.0 ng/L in Canada, Kota Kinabalu, Orebro, and Taipei. It was significantly high in Osaka (average was more than 1,000 ng/L, median was 48.6 ng/L), and it was more than 15 ng/L in Kyoto, Shenzhen, Khon Kaen, and Singapore. PFOA tends to be low in the natural area. As a further study, more detail surveys will be required in Osaka area.

Figure 3 shows PFOS and PFOA concentrations in tap water in 21 cities, 10 countries. PFOS was detected throughout the survey area in the range from 0.01 ng/L to 143.1 ng/L. Average concentration of PFOS in tap water



Fig. 2 PFOS and PFOA contamination of surface water in rivers

was less than 0.35 ng/L in Hanoi, Kunming, Kota Kinabalu, Khon Kaen, Johor Bahru, and Shimane. It was more than 10.0 ng/L in Bangkok and Taipei. PFOA was detected throughout the survey area in the range from 0.01 ng/L to 86.9 ng/L. Average concentration of PFOA in tap water was less than 0.20 ng/L in Kunming, Hanoi, Taipei, Kota Kinabalu, and Canada. It was more than 10 ng/L in Osaka and Okayama in Japan.



Fig. 3 PFOS and PFOA contamination of tap water

Some samples were collected in water purification plants with an ozonation tank and an activated carbon tank in the process, Japan. However, PFOS and PFOA concentrations of influent and effluent were similar. It suggests it might be difficult to remove PFOS and PFOA in trace levels by current water purification process.

64 samples were collected in influent of waste water treatment plants. PFOS was detected from 0.01 ng/L to 54.8 ng/L (average 14.4 ng/L, median 5.9 ng/L). PFOA was detected from 0.01 ng/L to 455.9 ng/L (average 84.7 ng/L, median 34.4 ng/L). 144 samples were collected in effluent of waste water treatment plants. PFOS was detected from 0.07 ng/L to 467.0 ng/L (average 28.4 ng/L, median 13.6 ng/L). PFOA was detected from 0.79 ng/L to 8006.6 ng/L (average 254.3 ng/L, median 55.9 ng/L). PFOS and PFOA of dissolved matter tends to increase in WWTPs (PFOS 2.3 times, PFOA 1.6 times). As a further study, continuous removal experiments for PFCs will be required.

Acknowledgements

Authors acknowledge Prof. Ruya Tasli, Dr. Mohamaed Pauzi, Dr. Yuntao Guan and Dr. Tadao MIZUNO. This research was supported by Grant-in-Aid for Scientific Research (Germinate 20656084), and NEDO(0410005).

Reference

1. Tanaka S, Fujii S, N.P.H.Lien, Nozoe M, Fukagawa H, W. Wirojanagud, A. Anton and G. Lindstrom, *Organohalogen Compounds*, 527-530 (2006), 2. Saito N, Sasaki K, Nakatome K, Harada K, Yoshinaga T, and Koizumi A, *Arch Environ. Contam. Toxicol.*, 2004;45:149.