CONTAMINATION OF PFOA AND PFOS IN THE RIVERS OF HYOGO PREF., JAPAN

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Abstract

The investigation was carried out to grasp the contamination of PFOA and PFOS in 40 rivers of Hyogo Prefecture, western Japan. PFOA was detected at about 40% of the monitoring points, mainly in urban rivers, and PFOS was detected at about 10% of the points.

The highest concentration of PFOA was detected in the downstream of Ina River in Hanshin area. It was presumed that the pollution was caused by a point source located in the upper stream of the tributary flowing through Osaka area.

On the other hand, the highest concentration of PFOS was detected in the second class river flowing through Hanshin area. In this area, there is no particular point source of PFOS such as airport using fluorinated fire fighting agents and fluorocarbon resin producing factory. For this reason, it was suggested that PFOS contamination from non-point source in this area.

Introduction

The environmental pollution of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) has become popular through the reports on the environmental problem for fluorochemical surfactants in Europe and USA. Also in Japan, a national-wide investigation for PFOA and PFOS have been carried out and widely distributed contamination has been clarified [1), 2)].

In the investigation report, high contaminations of PFOA and PFOS in Kinki Region were pointed out. The concentrations of PFOA and PFOS were 12ng/L and 1.1ng/L as geometric mean value of n=5, respectively, in river waters of Hyogo Pref., which levels were second - highest contamination, following the Osaka Pref. (PFOA: 40ng/L, PFOS: 12ng/L). Therefore, further investigation was planed to grasp the pollution levels of PFOA and PFOS in Hyogo Pref. precisely.

In this study, the contaminations of PFOA and PFOS were investigated in 40 rivers. And then the detail survey was followed in the area where high concentration was detected.

Materials and Methods

Surface waters were collected in 40 rivers distributed over the prefecture area in July or August in 2006. Sample pretreatment using solid phase extraction was performed based on the method by Sasaki et al [3)]. Analytical condition of LC/MS is shown in Table1. The quantification limits are 2.5ng/L for PFOA and 1.7ng/L for PFOS.

Table 1. Analitical condition for PFOS and PFOA with LC/MS

【HPLC】		【MS】		
Instrument	Agilent 1100	Instrument	Finnigan LCQ	
Column	Ascentis C18	Ionization	ESI	
	(15cm×4.6mm , pore size 5μm)	Polarity	Negative	
Mobile phase	A ; 10mM CH_3COONH_4/H_2O	Capillary temp.	275 ℃	
	B ; CH_3CN	Source voltage	5 kV	
(gradient condition)	B) 50% (0min) - 90% (9min) -	Capillary voltage	-20 V	
	- 50% (12min) - 50% (14min)	Tube lens voltage	10 V	
Flow rate	0.5 mL / min	N_2 gas flow rate	70 arb	
Oven temp.	40 ℃	SIM ion	PFOS	499
Injection volume	10 μL		PFOA	413
			PFOA -$^{13}C_2$	415

Results and Discussion

In the 40 rivers, PFOA was detected at 15 points, and the highest concentration was 410ng/L, detected in the first class river which flows through Hanshin area. On the other hand, PFOS was detected at 4 points, and the highest concentration was 61ng/L, detected in the second class river which flows through the same area. The geometric mean concentrations of each compound were 17ng/L of PFOA and 2.1ng/L of PFOS. The concentration levels resembled those of a national-wide investigation[1)].

The histograms of each concentration are shown in Fig.1. As for PFOA, 60% of all investigation points were less than the quantification limit. Contamination level of detected points was almost low and the points were concentrated in urban area. On the other hand, as for PFOS, 90% of all investigation points were less than the quantification limit.

At the two points where high concentrations of PFOA and PFOS were detected, further investigation was carried out to clarify the causes.

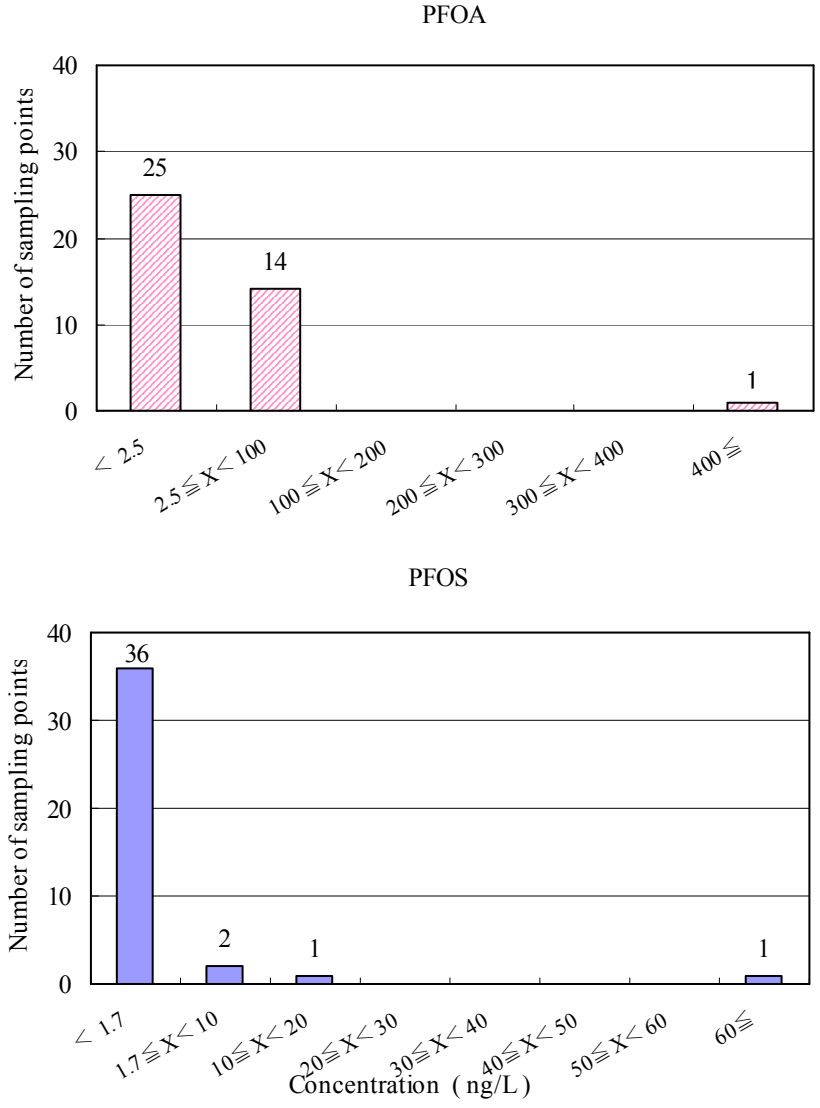

Fig.1. Frequency distribution of PFOA and PFOS concentrations in rivers of Hyogo Pref.

High contamination area for PFOA

The highest concentration of PFOA was 410ng/L at point No.1 in the Ina River (Fig. 2). This contamination level was almost same as the situation reported in the recent newspapers. The detail survey in this area was carried out in August in 2006. Further sampling points and the concentrations of 2 fluorochemicals are shown in Fig.2 and Fig. 3, respectively.

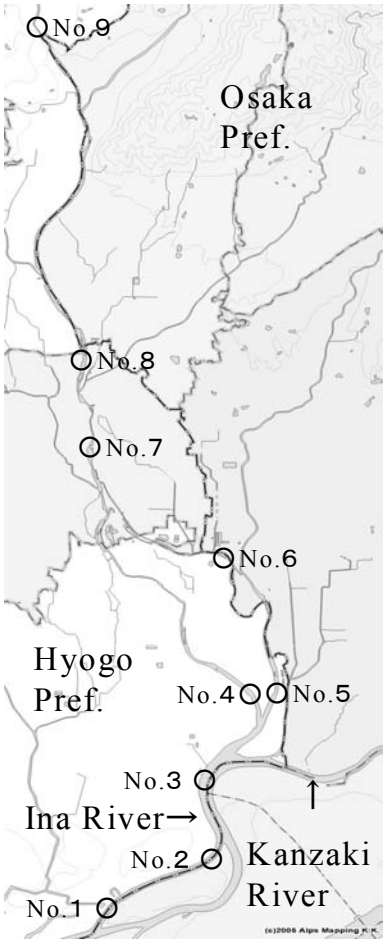

Fig.2. Sampling point in Ina River basin

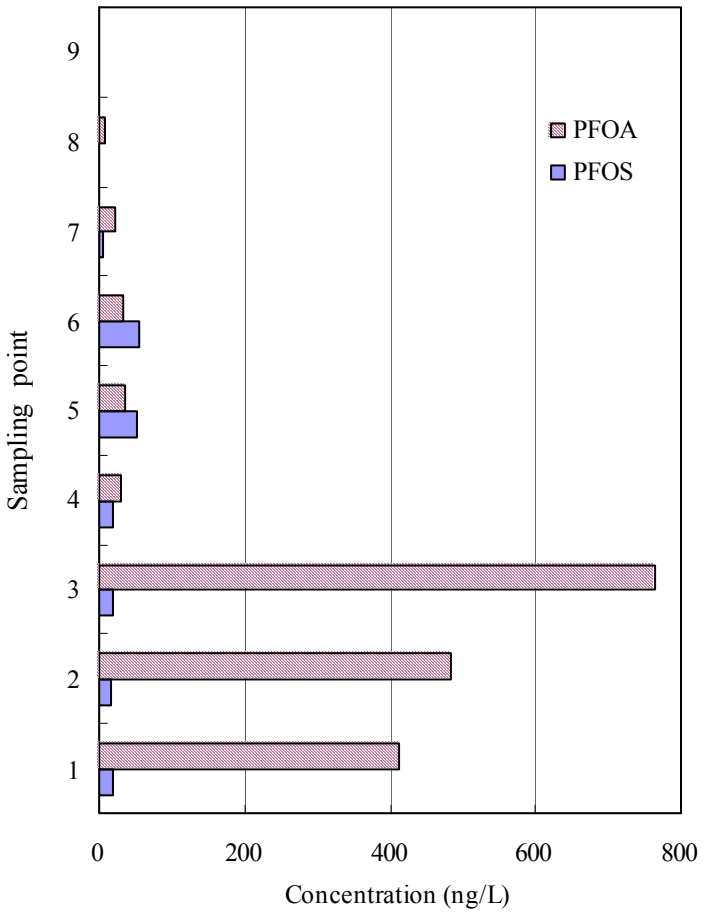

Fig.3. Concentrations of PFOA and PFOS in the Ina River

The highest point for PFOA was No.3, located in the downstream at the junction of Ina River and Kanzaki River. This point is located in the prefectural boundary between Hyogo and Osaka. PFOS at upstream points (No.4 – No.9) in Hyogo area were lower, compare with the downstream, in which the concentrations were from N.D. (not detected) to 35ng/L.

According to the references[1), 2)] and the newspapers, there is a highly polluted spot in the upper reaches of Kanzaki River in Osaka area. Therefore, it was presumed that the pollution of PFOA in the downstream was caused by the inflow of Kanzaki River from Osaka area.

From this investigation, 2 types of the pollution were found. One was the high contamination type caused by some point sources and another was the lower contamination type, which pollution spread in urban areas. This is considered non-point contamination.

High contamination area for PFOS

The detail survey was carried out in the urban river in November 2006, where high concentration of PFOS was detected. And then the investigation was followed in the rainwater drainage flowing into this river in January and March 2007.

Fig.4 shows the concentration profiles of PFOS in their urban river and rainwater drainage.

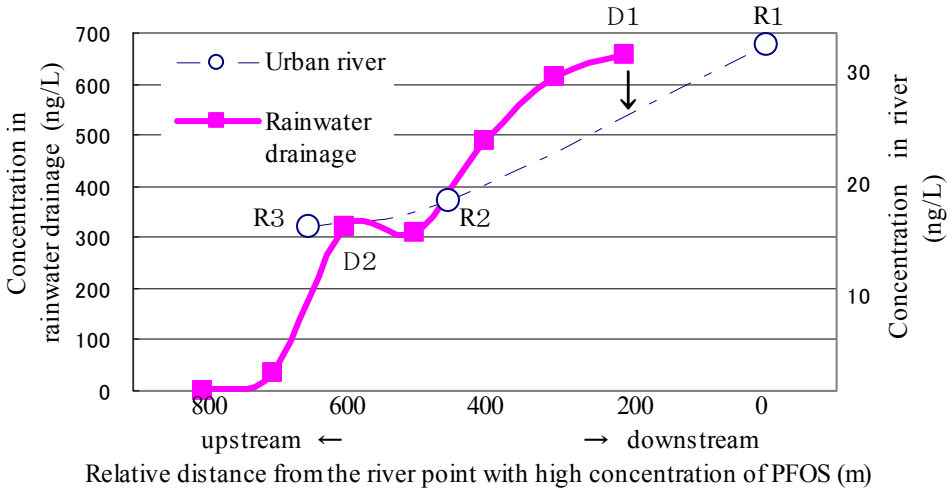

Fig.4. Concentrations of PFOS in urban river and rainwater drainage in Hanshin area

The highest concentration of 650ng/L was observed at D1 in the rainwater drainage. In the drainage, PFOS was mainly detected in the downstream of D2 with relative distance of 400m from the inflow point.

On the other hand, in this river, there was no point with higher concentration of PFOS in upper reaches of R1. Here is the commercial and residential area and there is no particular point source of PFOS such as airport using fluorinated fire fighting agents and factory producing fluorocarbon resin. In addition, this drainage receives rainwater only.

From the result, it was suggested that the contamination of PFOS was derived from the inflow of rainwater through the drainage. There is concern that PFOS pollution from non-point source is widely distributed in urban areas.

References

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