

CONTAMINATION OF PERFLUORINATED COMPOUNDS IN THE RIVER WATER OF HYOGO PREF., JAPAN

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Abstract

One Liter of surface water was sampled at monitoring points. In 2007, 54 river water, 14 sea water, and 15 sewage works effluent samples were collected. In 2008, 40 river water samples were collected. The analysis was carried out using LC/MS/MS. The investigation was carried out to grasp the perfluorooctanoate (PFOA) and Perfluorooctane sulfonate (PFOS) contamination of environmental waters in Hyogo Prefecture, Japan. PFOA concentrations and detected ratios (number of detected samples / all samples) were higher than PFOS. In 2008, the congener analysis was carried out using LC/MS/MS. PFOA was detected as the predominant congener in a lot of sampling points. In the Tatsumi Bridge, congener distribution was characteristic. The concentration of PFHxA was about 20 times higher than PFOA. Meanwhile, the PFOA concentration was decreasing. It is thought that the convert to product with a short carbon chain is reflected in these rivers. In coastal area, PFOA were detected and the concentrations were higher at closed-off section of the Osaka bay observed than other area. Therefore, it was thought that the influence from the PFOA source appeared through the river. In the sewage works effluent, PFOA and PFOS were detected of all samples, and the concentration level is higher than environmental water samples.

Introduction

Perfluoroalkyl sulfonates (PFASs) and Perfluorocarboxylic acids (PFCAs) are used primarily as surfactant compounds in consumer based applications. PFOS and PFOA have received the most attention and have been detected in human serum¹, freshwater and marine biota, and surface water. The stability that makes fluorinated surfactants so desirable appears to preclude any degradation or metabolism, and contributes to the global bioaccumulation and persistence of PFOS and PFOA.

The 2010/15 PFOA Stewardship Program was launched in 2006 by the U.S. Environmental Protection Agency (EPA) and eight international fluoropolymer and telomer manufacturers and processors doing business in the United States. The 2010/15 PFOA Stewardship Program was launched in 2006 by the U.S. Environmental Protection Agency (EPA) and eight international fluoropolymer and telomer manufacturers and processors doing business in



Figure1 The sampling points Geography. The filled circles show sampling points of river in Hyogo prefecture region.

Table1 Analytical condition for PFOS and PFOA with LC/MS

LC conditions	Condition 2
Instrument:	ACQUITY UPLC (waters)
Column:	UPLC BEH C ₁₈ 2.1×50mm
Retention gap Column:	UPLC BEH C ₁₈ 2.1×100mm
MobilePhase:	A : 10mM Ammonium Acetate aq B : CH ₃ CN
Gradient :	B : 1%(0min) 95%(8min) 1%(8.1min)
Flow rate/Column temp./Injection volume:	0.3 mL/min / 40 °C / 5µL
MS/MS conditions	
Instrument:	ACQUITY TQD(waters)
Ionisation Mode:	ESI (Negative)
Source and Desolvation temp:	120 °C / 300 °C
Capillary Voltage:	2 kV
Cone and Desolvation gas flow:	20 L/Hr / 800 L/Hr
Collision Gas Flow:	0.1 mL/Min
Precursor/ Product Ion[m/z]	PFOS :499.0/79.0, PFOA :413.0/368.7
Cone Voltage[V]	PFOS : 20, PFOA :55
Colision Energy[eV]	PFOS : 20, PFOA :40
LC conditions	Condition 3
Instrument	Agilent 1100
Column	TOSOH ODS100S (15cm×2mm, pore size 5µm)
Mobile phase	A ; 2mM NH ₄ HCO ₃ /H ₂ O B ; CH ₃ CN
(gradient condition)	B)10% (0min) - 10% (4min) - 100% (9min) - 100% (13min)
Flow rate/Oven temp./Injection volume	0.2 mL / min / 40 oC / 5 µL
MS/MS conditions	
Instrument	Applied Biosystems API2000
Ionization (Polarity)	ESI (Negative)
Heater gas temp.	550 °C
Ionspray voltage	-4.5 kV
Declustering potential/Collision energy	-5 ~ -96 V / -8 ~ -86 V
MRM	PFOS 499/80, 499/99, 499/119 PFOA 413/169, 413/369 PFOS- ¹⁸ O ₂ 504/84, 504/103 PFOA- ¹³ C ₄ 417/169, 417/372

the United States. Some manufacturers have converted to the product with a short carbon chain.

We had been investigated PFOS and PFOA concentration of the water environment in the Hyogo prefecture from 2006². In addition to this, congener distributions with different length of the carbon chain are investigated on water environment in Hyogo prefecture.

Materials and Methods

Sample collection:
One Liter of surface water was sampled at monitoring points in Hyogo prefecture region. In 2007, 54

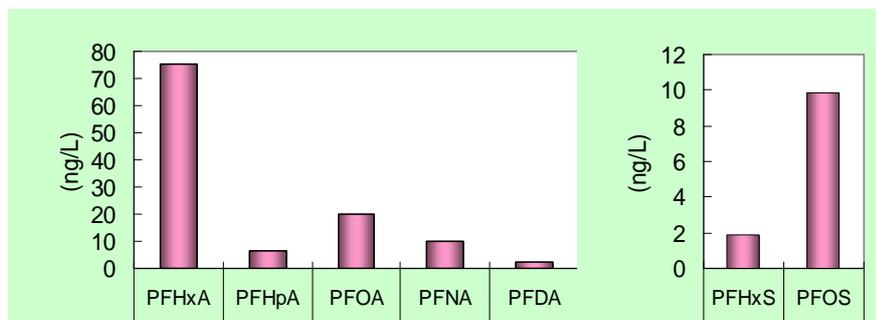


Figure2 Average of perfluorinated compounds concentrations(ng/L) in river water of Hyogo prefecture region in 2008. (n=40, all samples)

river water samples were collected on May or June and 14 sea water samples were collected on July. In 2008, 40 river water samples were collected on September. 200mL of water were used for analysis and stored in 4°C until analysis.

Extraction and cleanup: Sample pretreatment using solid phase extraction was performed based on the method by Sasaki et al.³

Analysis: Analytical condition of LC/MS/MS is shown in literature² (*condition1*) and Table1 (*condition2 and 3*). The quantification limits are 3ng/L for PFOA and 2ng/L for PFOS. In 2008, PFOS, PFOA and furthermore PFHxA, PFHpA, PFNA, PFDA and PFHxS were analyzed.

PFCs standard solutions: PFCAs mixed standards solutions (PFC-MXA) and PFASs mixed standards solutions (PFS-MXA) were obtained from Wellington Laboratory Inc. (Canada). ¹³C Labeled PFCAs and PFASs mixed standards solution (MPFAC-MXA) was obtained from Wellington Laboratory Inc. (Canada), used for surrogate standard.

Results and Discussion

PFCAs Congener distribution: Figure2 shows average of perfluorinated compounds concentrations (ng/L) in river water of Hyogo prefecture region in 2008. (n=40, all samples) However, PFHxA was predominant congener, there were only eight sampling points that were more or equal the concentration of PFHxA compared with PFOA. Figure3 shows congener distribution of perfluorinated carboxylic acids (C6-C10) in river water of Hyogo prefecture region in 2008. (concentration unit is ng/L) (A) is a average graph calculated except the Tatsumi bridge. (n=39) (B) is result of The Tatsumi bridge (The Samondo river). (C) is result of The Nozoe bridge (The Kise river). (D) is result of The Chidori bridge (The Hokkesan-tani river). In the Tatsumi Bridge, congener distribution was characteristic. The concentration of PFHxA was about 20 times higher than PFOA. It is thought that the convert to product with a short carbon chain is reflected in these rivers. PFOA was detected as the predominant congener in a lot

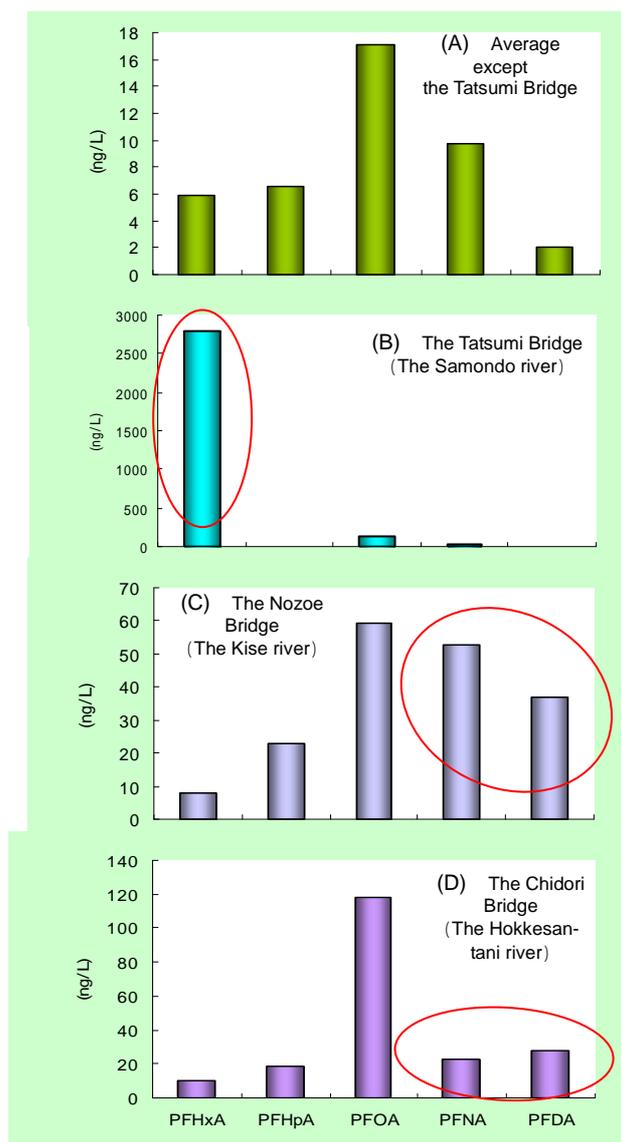


Figure3 Congener distribution of perfluorinated carboxylic acids (C6-C10) in river water of Hyogo prefecture region in 2008. (concentration unit is ng/L)
 (A) is a average graph calculated except the Tatsumi Bridge. (n=39)
 (B) is result of The Tatsumi Bridge (The Samondo river). (C) is result of The Nozoe Bridge (The Kise river). (D) is result of The Chidori Bridge (The Hokkesan-tani river).

Table2 Average of PFOA and PFOS concentrations(ng/L) of river water of Hyogo prefecture region from 2006 to 2008.

Compound (year)	(2006) ²	PFOA (2007)	(2008)	(2006) ²	PFOS (2007)	(2008)
number	40	54	40	40	54	40
detected ratio (%)*	38	70	70	10	63	58
max (ng/L)	410	670	140	61	44	160
min (ng/L)	<3	<3	<3	<2	<2	<2
average (ng/L)	17	60	20	2.2	6.6	9.5

* Ratio of detected sample to all samples (%)

**The quantitative limits were <3 (PFOA) and <2 (PFOS).

of sampling points. There were sampling

points where PFNA and/or PFDA ratio to PFOA had been increased. There were 5 sampling points include the Nozoe Bridge (C) and the Chidori Bridge (D).

PFASs Congener distribution: In PFASs congener pattern, PFOS was predominant congener in most sampling points.

River water concentrations variation: Table2 and Figure4 shows Average of PFOA and PFOS concentrations (ng/L) in river water of Hyogo prefecture region from 2006 to 2008. In figure4, Upper part is a graph calculated all samples (40 samples). Under part is a graph calculated the 17 samples measuring 3 years in a row. In this result, PFOA concentrations and detected ratios were higher than PFOS. In highest contaminant point, the Tatsumi Bridge, PFOA concentration are decreasing. Therefore, it seems that average concentration of PFOA is decreasing. Meanwhile, a tendency of PFOS concentration is not clear. Yoshida et al² reported that there were PFOS contamination from non-point source, there is not clear about the source of PFOS. For this reason, the further investigation is necessary in the point where the concentration is comparatively high.

Sea water and sewage works effluents: Table3

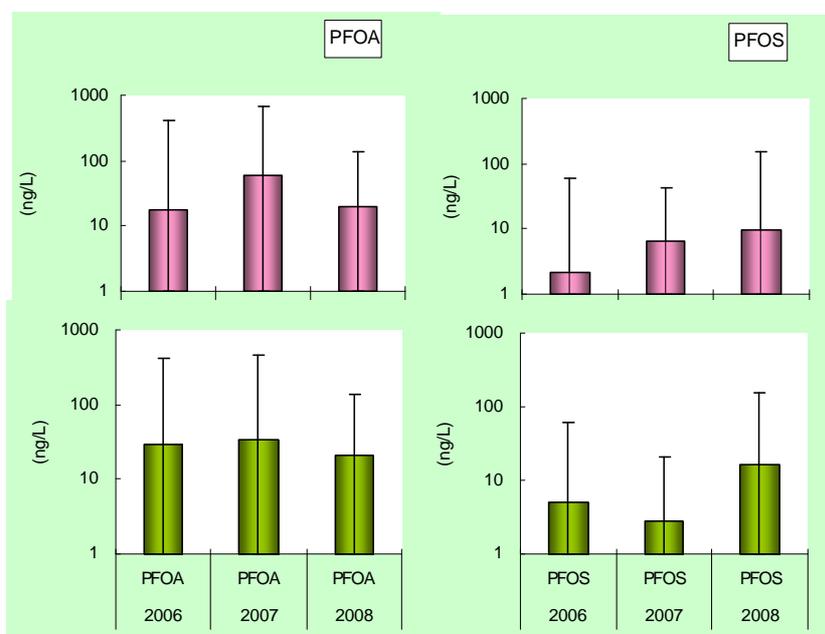


Figure4 Average of PFOA and PFOS concentrations(ng/L) in river water of Hyogo prefecture region from 2006 to 2008. Upper part is a graph calculated all samples. Under part is a graph calculated the 17 samples measuring 3 years in a row.

shows Average of PFOA and PFOS concentrations

(ng/L) of sea water and sewage works of Hyogo prefecture region in 2007. PFOS were not detected at all sea sampling points. PFOA were detected and the concentrations were higher at closed-off section of the Osaka bay observed than other region. Therefore, it was thought that the influence from the PFOA source appeared through the river. In the sewage works effluent, PFOA and PFOS were detected from all samples, and the concentration level is higher than environmental waters.

Table3 Average of PFOA and PFOS concentrations(ng/L) of sea water and sewage works of Hyogo prefecture region in 2007.

Compound (year)	Sea Water PFOA	Water PFOS	Sewage Works PFOA	PFOS
number	14	14	15	15
detected ratio (%)*	57	0	100	100
max (ng/L)	50	<2	100	150
min (ng/L)	<3	<2	13	3
average (ng/L)	7.5	<2	43	25

* Ratio of detected sample to all samples (%)

**The quantitative limits were <3 (PFOA) and <2 (PFOS).

Conclusion

PFOA was detected as the predominant congener in a lot of sampling points. There was a sampling point where PFHxA had been in a high concentration detected. There were sampling points where PFNA and/or PFDA ratio to PFOA had been increased. It will investigate in detail in these sampling points in the future. In coastal area, PFOA were detected and the concentrations were higher at closed-off section of the Osaka bay observed than other area. In the sewage works effluent, PFOA and PFOS were detected of all samples, and the concentration level is higher than environmental water samples.

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