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

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Abstract

In this research, we investigated contamination of Perfluorinated compounds (PFCs) in the river and the sea in Hyogo prefecture region, Japan. The analyzed compounds were Perfluoroalkyl sulfonates (PFASs: PFBS, PFHxS, PFOS, PFDS) and Perfluorocarboxylic acids (PFCAs: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA). The analysis was carried out using LC/MS/MS. The range of PFOS and PFOA concentrations in the river water samples were <1～49ng/L and <1～470ng/L. In addition, the range of PFOS and PFOA concentrations in the sea water samples were <1～4.8ng/L and <1～62ng/L. However, high concentration of PFHxA that has shorter carbon chain than PFOA, alternative material of PFOA, were detected in a concentration of 6200 ng/L in the downstream of the fluorine chemistry factory of Osaka prefecture. In the sea, the concentrations of PFHxA were different between Osaka bay (22ng/L～670ng/L) and Harima-nada (<1～36ng/L). In addition, indicating an inverse association between the concentration of PFHxA in the sea water samples and the distance from the mouth of Kanzaki-river, it suggested that the effect of contamination from the closed-off section of bay was large.

Introduction

PFASs and 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 serum[1], 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. 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 2006 to 2008[2,3]. In addition to this, congener distributions with different length of the carbon chain are

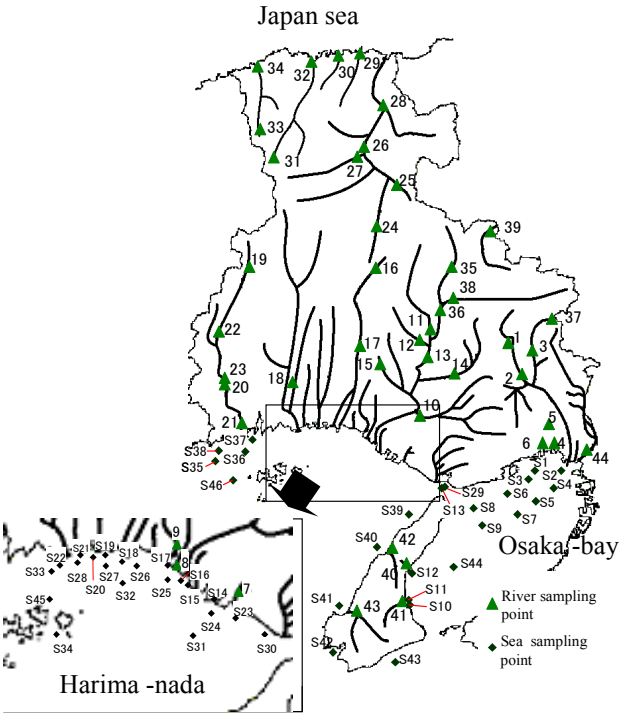

Fig.1 The sampling points Geography.
The filled circles and triangle show sampling points of river and sea water in Hyogo prefecture region.

investigated on water environment in Hyogo prefecture.

Table1 Analytical condition for PFASs and PFCAs with LC/MS/MS.

Instrument	: ACQUITY UPLC (waters)
Column	: UPLC BEH C18 2.1×50mm
Retention gap Column	: UPLC BEH C18 2.1×100mm
Mobile Phase	: A: 10mM Ammonium Acetate aq B : Acetonitrile
Gradient	: 0.0→9.0min B : 1→95% 9.0→9.1 B : 95→1%
Flow rate	: 0.3 mL/min
Column temp.	: 50℃
Injection volume	: 5μL
Instrument	: ACQUITY TQD (waters)
Ionization Mode	: ESI(-)
Source temp	: 120℃
Desolvation temp	: 300℃
Capillary voltage	: 2 kV
Cone gas flow	: 20 L/Hr
Desolvation gas flow	: 800 L/Hr
Collision Gas Flow	: 0.1 mL/Min

Materials and Methods

Sample collection: One Liter of surface water was sampled at monitoring points in Hyogo prefecture region. (see Fig.1) In 2009, 44 river water samples were collected on July or August and 46 sea water samples were collected on July or August. 100-200mL 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 [4].

Analysis: Analytical condition of LC/MS/MS is shown in Table1. The analyzed compounds and quantification ion were same as previously reported[5]. The quantification limits are 1ng/L for PFASs and 1ng/L for PFCAs. All blank tests were under the detection limit.

PFCs standard solutions: PFCAs mixed standards solutions (PFC-MXA) and PFASs mixed standards solutions (PFS-MXA) were obtained from Wellington Laboratory Inc. (Canada). ^{13}C Labeled PFCAs and PFASs mixed standards solution (MPFAC-MXB) was obtained from Wellington Laboratory Inc. (Canada), used for surrogate standard. $^{13}C_8$PFOA was obtained from Wellington Laboratory Inc. (Canada), used for syringe spike standard.

Results and Discussion

PFCs congener in river water: Table2 shows PFCs concentrations (ng/L) in river water of Hyogo prefecture region in 2009. (n=44, 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. In the Tatumi 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 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 and the Chidori Bridge.

River water concentrations variation: 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 al[2] 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.

PFCs congeners in Sea water: Table3 shows PFCAs and PFASs concentrations (ng/L) of sea water of Hyogo prefecture region in 2009. PFOS was detected only one 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.

Relationship between PFCAs concentrations and distance: Fig.2 and 3 shows PFHxA or PFOA concentrations

(ng/L) and distance from the mouth of Kanzaki River. Kanzaki River runs for closed-off section of the Osaka bay. In addition, indicating an inverse association between the concentration of PFHxA in the sea water samples and the distance from the mouth of Kanzaki-river, it suggests that the effect of contamination from the closed- off section of bay is large.

Conclusion

The investigation to understand the PFC pollution was conducted at 44 sampling points of river and 46 sampling points of Seto-inland sea in Hyogo prefecture region.

PFOA was detected as the predominant congener in a lot of river sampling points. There was a sampling point where PFHxA had been in a high concentration detected. There was sampling point where the homologue pattern had been different from other sampling points, detected from PFHpA to PFUnDA. It will investigate in detail in these sampling points in the future.

In coastal area, PFOA was detected as the predominant congener in a lot of sampling points. The range of PFHxA concentrations was deferent in 22 to 670ng/L at Osaka bay area and under the 1 to 36ng/L at Harima-nada area. PFOA were detected and the concentrations were higher at closed-off section of the Osaka bay observed than other area.

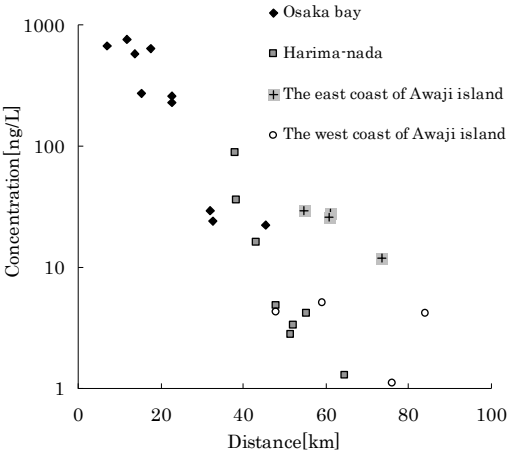

Fig.2 Relation ship between concentration of PFHxA in seawater samples and distance from the mouth of Kanzaki river.

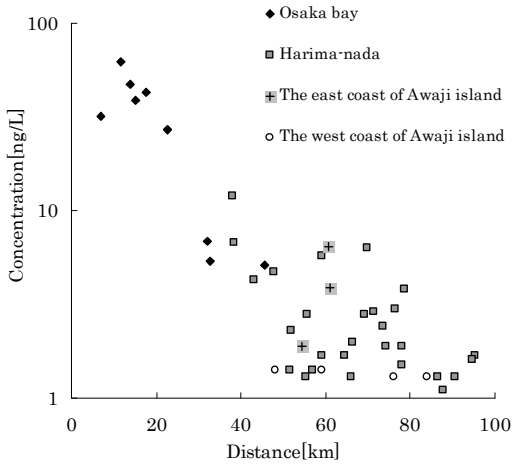

Fig.3 Relation ship between concentration of PFOA in seawater samples and distance from the mouth of Kanzaki river.

Acknowledgement

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Table2 PFCs concentrations of river water samples in Hyogo region and loading amount PFCs at sampling

Point NO.	Sampling point	Concentration[ng/L]													
		PFBS	PFHxS	PFOS	PFDS	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
1	Oohashi br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2	Sanda br.	<1	<1	<1	<1	<1	<1	<1	3.9	2.7	<1	<1	<1	<1	<1
3	Kobe ryousui kansokuchi	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4	miyagawa br.	<1	<1	49	<1	<1	<1	<1	49	<1	<1	<1	<1	<1	<1
5	Water supply source intake (ashiya river)	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
6	Narihira br.	<1	<1	<1	<1	<1	<1	<1	7.8	<1	<1	<1	<1	<1	<1
7	Nozoe br.	<1	<1	<1	<1	<1	<1	<1	29	6.7	<1	<1	<1	<1	<1
8	Chidori br.	<1	<1	<1	<1	<1	<1	6.9	310	52	100	87	<1	<1	<1
9	Higasa hodoukyou	<1	<1	<1	<1	<1	<1	<1	4.3	4.2	<1	<1	<1	<1	<1
10	Minokawa br.	<1	<1	<1	<1	<1	<1	<1	7.5	<1	<1	<1	<1	<1	<1
11	Kasuga br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
12	Iwai br.	<1	<1	<1	<1	<1	<1	<1	<1	12	<1	<1	<1	<1	<1
13	Heian br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
14	Eizoku br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
15	Hojo br.	<1	<1	<1	<1	<1	<1	<1	<1	1.7	<1	<1	<1	<1	<1
16	Mayumi br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
17	Kanzaki br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
18	Nakai br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
19	Muro br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
20	Kumami br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
21	Sakoshi br.	<1	<1	<1	<1	<1	<1	<1	2.8	<1	<1	<1	<1	<1	<1
22	Sakata br.	<1	<1	<1	<1	<1	<1	<1	1.5	<1	<1	<1	<1	<1	<1
23	kenbu br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
24	Tataragi br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
25	Tamaki br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
26	Kamioda br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
27	Suwa br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
28	Tenjin br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
29	Takeno shin br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
30	Sadu br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
31	Hosono br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
32	Yura br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
33	Hanakuchi br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
34	Kiyotomi br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
35	Nishiki br.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
36	Ihara br.	<1	<1	<1	<1	<1	<1	<1	3.4	<1	<1	<1	<1	<1	<1
37	Sakashita br.	<1	<1	<1	<1	<1	<1	<1	2.4	<1	<1	<1	<1	<1	<1
38	Yamazaki br.	<1	<1	<1	<1	<1	<1	<1	1.4	<1	<1	<1	<1	<1	<1
39	Hirota br.	<1	<1	<1	<1	<1	<1	2.5	3.1	<1	<1	<1	<1	<1	<1
40	Shidu br.	<1	<1	<1	<1	<1	<1	<1	52	<1	<1	<1	<1	<1	<1
41	Ushio br.	<1	<1	<1	<1	<1	7.2	<1	15	<1	<1	<1	<1	<1	<1
42	Water supply source intake (gunge river)	<1	<1	<1	<1	<1	<1	<1	20	<1	<1	<1	<1	<1	<1
43	Wakita br.	<1	<1	<1	<1	<1	<1	<1	5.7	<1	<1	<1	<1	<1	<1
44	Tatsumi br.	<1	<1	<1	<1	<1	6200	<1	470	<1	<1	<1	<1	<1	<1
	Max	-	-	49	-	-	6200	6.9	470	52	100	87	-	-	-
	Detected number	0	0	1	0	0	2	2	18	6	1	1	0	0	0

Table3 PFCs concentrations of sea water samples in Hyogo region.

Point NO.	Concentration[ng/L]													
	PFBS	PFHxS	PFOS	PFDS	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
S1	<1	<1	<1	<1	<1	570	<1	47	4.3	<1	<1	<1	<1	<1
S2	<1	<1	<1	<1	<1	670	<1	32	6.4	<1	<1	<1	<1	<1
S3	<1	<1	<1	<1	<1	270	<1	39	15	<1	<1	<1	<1	<1
S4	<1	<1	4.8	<1	<1	760	<1	62	15	<1	<1	<1	<1	<1
S5	<1	<1	<1	<1	<1	640	<1	43	9.9	<1	<1	<1	<1	<1
S6	<1	<1	<1	<1	<1	260	<1	27	8	<1	<1	<1	<1	<1
S7	<1	<1	<1	<1	<1	230	<1	27	3.7	<1	<1	<1	<1	<1
S8	<1	<1	<1	<1	<1	29	<1	6.9	1.2	<1	<1	<1	<1	<1
S9	<1	<1	<1	<1	<1	24	<1	5.4	1.1	<1	<1	<1	<1	<1
S10	<1	<1	<1	<1	<1	28	<1	3.9	<1	<1	<1	<1	<1	<1
S11	<1	<1	<1	<1	<1	26	<1	6.4	<1	<1	<1	<1	<1	<1
S12	<1	<1	<1	<1	<1	29	<1	1.9	<1	<1	<1	<1	<1	<1
S13	<1	<1	<1	<1	<1	36	<1	6.8	1.3	<1	<1	<1	<1	<1
S14	<1	<1	<1	<1	<1	2.8	<1	1.4	<1	<1	<1	<1	<1	<1
S15	<1	<1	<1	<1	<1	<1	<1	2.8	<1	<1	<1	<1	<1	<1
S16	<1	<1	<1	<1	<1	<1	<1	1.4	<1	<1	<1	<1	<1	<1
S17	<1	<1	<1	<1	<1	<1	<1	5.7	<1	<1	<1	<1	<1	<1
S18	<1	<1	<1	<1	<1	<1	<1	2	5.1	<1	<1	<1	<1	<1
S19	<1	<1	<1	<1	<1	<1	<1	6.3	<1	<1	<1	<1	<1	<1
S20	<1	<1	<1	<1	<1	<1	<1	2.9	<1	<1	<1	<1	<1	<1
S21	<1	<1	<1	<1	<1	<1	<1	2.4	<1	<1	<1	<1	<1	<1
S22	<1	<1	<1	<1	<1	<1	<1	3	<1	<1	<1	<1	<1	<1
S23	<1	<1	<1	<1	<1	4.9	<1	4.7	2.7	<1	<1	<1	<1	<1
S24	<1	<1	<1	<1	<1	3.3	<1	2.3	<1	<1	<1	<1	<1	<1
S25	<1	<1	<1	<1	<1	<1	<1	1.7	<1	<1	<1	<1	<1	<1
S26	<1	<1	<1	<1	<1	1.3	<1	1.7	<1	<1	<1	<1	<1	<1
S27	<1	<1	<1	<1	<1	<1	<1	2.8	<1	<1	<1	<1	<1	<1
S28	<1	<1	<1	<1	<1	<1	<1	1.9	<1	<1	<1	<1	<1	<1
S29	<1	<1	<1	<1	<1	88	<1	12	4.1	<1	<1	<1	<1	<1
S30	<1	<1	<1	<1	<1	16	<1	4.3	<1	<1	<1	<1	<1	<1
S31	<1	<1	<1	<1	<1	4.2	<1	1.3	<1	<1	<1	<1	<1	<1
S32	<1	<1	<1	<1	<1	<1	<1	1.3	<1	<1	<1	<1	<1	<1
S33	<1	<1	<1	<1	<1	<1	<1	1.9	<1	<1	<1	<1	<1	<1
S34	<1	<1	<1	<1	<1	<1	<1	1.5	<1	<1	<1	<1	<1	<1
S35	<1	<1	<1	<1	<1	<1	<1	1.7	<1	<1	<1	<1	<1	<1
S36	<1	<1	<1	<1	<1	<1	<1	1.1	<1	<1	<1	<1	<1	<1
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S39	<1	<1	<1	<1	<1	4.3	<1	1.4	<1	<1	<1	<1	<1	<1
S40	<1	<1	<1	<1	<1	5.1	<1	1.4	<1	<1	<1	<1	<1	<1
S41	<1	<1	<1	<1	<1	1.1	<1	1.3	<1	<1	<1	<1	<1	<1
S42	<1	<1	<1	<1	<1	4.2	<1	1.3	<1	<1	<1	<1	<1	<1
S43	<1	<1	<1	<1	<1	12	<1	<1	<1	<1	<1	<1	<1	<1
S44	<1	<1	<1	<1	<1	22	<1	5.1	<1	<1	<1	<1	<1	<1
S45	<1	<1	<1	<1	<1	<1	<1	3.8	<1	<1	<1	<1	<1	<1
S46	<1	<1	<1	<1	<1	<1	<1	1.3	<1	<1	<1	<1	<1	<1
Max	-	-	4.8	-	-	760	-	62	15	-	-	-	-	-
Detected number	0	0	1	0	0	26	0	45	13	0	0	0	0	0