

PERFLUORINATED COMPOUNDS IN GROUNDWATER FROM TOKYO, JAPAN

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Introduction

Perfluorinated surfactants (PFCs) such as Perfluorooctane sulfonate (PFOS) and Perfluorooctanoate (PFOA) are used in fluoropolymer manufacture and fire-fighting foams. PFCs and their precursors are also included in carpeting waxes and textiles. In May 2009, PFOS was included on the global list of persistent organic pollutants (POPs) under Stockholm Convention¹. Regarding PFOA, the 2010/2015 PFOA Stewardship Program emphasizes that no later than 2010, a 95% reduction, as measured from a year 2000 baseline, must be achieved in facility emissions for all media of PFOA, precursor chemicals that can break down to PFOA, related higher homologue chemicals, and product content levels of these chemicals². In Japan, the PFCs surveillance at public water areas, PFOS and PFOA were frequently detected in river water³. These chemicals were detected and its ranges in groundwater were similar to those in rivers and wastewater in urban area of Tokyo⁴. The urban area of Tokyo is one of the most urbanized in Asia. PFOS was detected at the higher concentration in the Tama river than the average concentration of nationwide survey³. The catchment basin of the Tama river is the suburbs of Tokyo and we conducted a survey of groundwater from the whole area of Tokyo include urban and the suburbs.

Material and Methods

Samples

We collected 65 groundwater samples in the Tokyo metropolitan area in FY 2010. Samples were collected and stored in 250 mL polypropylene bottles. Sampling point of groundwater shown in Figure-1.

Standards

Standard compounds used for this study are PFHpS standard solution (50 µg/mL methanol solution) and two standard mixture solutions produced by Wellington Laboratories Inc. (Ontario, Canada). Each mixture solution contained 11 perfluorocarboxylic acids (PFAC-MXB: each compound contained 2 µg/mL methanol solution), and 9 mass-labeled perfluoro compounds (MPFAC-MXA: each compound contained 2 µg/mL methanol solution). Before analyses, PFHpS and PFAC-MXB were mixed and diluted to 200 ng/mL with methanol. Then, MPFAC-MXA was diluted to 200 ng/mL with methanol for use as an internal standard mixture. Table 1 presents a list of standard mixtures and their constituent compounds.

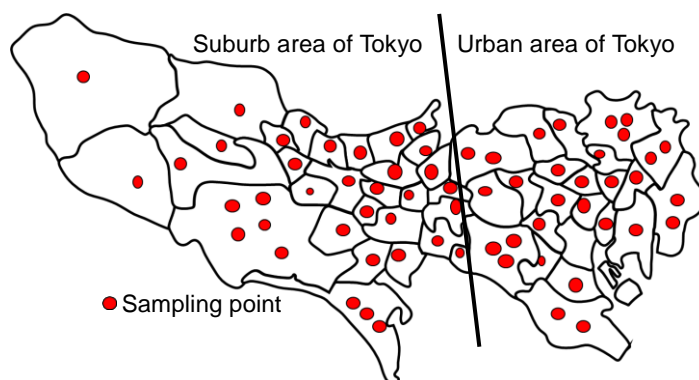


Fig.1 Sampling point of groundwater

Analysis of samples

Water samples were filtered using 0.4 µm glass fiber filtration paper (GB-140; Toyo Roshi Kaisha Ltd., Tokyo, Japan). Before solid phase extraction, 20 µL of internal standard mixture was added to filtrate. For the solid phase extraction column, a weak anion exchange cartridge column (OASIS[®]-WAX Plus; Waters Corp., Milford USA) was used. The cartridge was preconditioned with 5 mL of methanol, 10 mL of ultrapure water, and 5 mL of aquatic solution of formic acid (pH 4). The solid phase was extracted at 5 mL/min. After extraction, the cartridge column was washed with 50 mL of ultrapure water and 30 mL of methanol. Subsequently, it was eluted with 5 mL of 1% ammonium hydroxide in methanol. After elution, it was concentrated by N₂ purge to 1 mL, adjusted to 2 mL with 50% methanol in H₂O, and filtered through a 0.2 µm nylon membrane filter. The final sample was analyzed using LC/MS/MS (Premier XE; Waters Corp., Milford USA).

Table 1 Compounds in each standard solution

Standard	Compounds in each standard solution
PFHpS	PFHpS (50 µg/mL)
PFAC-MXB	PFBS, PFHxS, PFOS, PFDS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrA, PFTdA, PFHxDA, PFODA (each compound contained 2 µg/mL)
MPFAC-MXA	¹³ C ₄ -PFBA, ¹³ C ₂ -PFHxA, ¹³ C ₄ -PFOA, ¹³ C ₅ -PFNA, ¹³ C ₂ -PFDA, ¹³ C ₂ -PFUdA, ¹³ C ₂ -PFDoA, ¹⁸ O ₂ -PFHxS, ¹³ C ₄ -PFOS (each compound contained 2µg/mL)

Instrumentation and analytical conditions of LC/MS/MS

Separation was achieved on an L-column2 ODS (2.1 × 150 mm, 3 µm; CERI, Saitama, Japan) with a guard column (L-column2 C18: 2.1 × 50 mm, 3 µm). The column oven was set to 40°C. Separation was conducted using a mobile phase of 10 mM of ammonium acetate in water (solvent A)/acetonitrile (solvent B) at the flow rate of 0.2 mL/min. The gradient profile of the mobile phase was as follows: 0–5 min with maintained solvent B at 45%, 5–10 min linear increase solvent B to 95%, 10–15 min return to solvent B 45%, and 15–20 min maintained as constant. The capillary voltage was adjusted to 0.5 kV.

Results and Discussion

The method detection limit (MDL) was confirmed. After adding the standard mixture methanol solution to ultrapure water to 2 ng/L as a concentration in 250mL of water sample, the method detection limit was calculated based on recovery experiments repeated seven times. Table 2 presents those results.

Table 2 Method Detection Limits for respective compounds (ng/L)

Compound	PFBS	PFHxS	PFHpS	PFOS	PFDS
MDL	1.2	1.9	1.3	1.3	1.7

Compound	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTrA
MDL	1.3	1.3	0.7	1.0	1.0	1.3	1.3	1.0

Table 3 shows the results analysis of PFCs in groundwater from Tokyo. Samples No. 1-No.30 were collected in urban area and others were collected in suburbs. All PFCs that measured in this study were detected and only 9 samples were not included any PFCs. The detection rate of PFOS and PFOA considered major PFCs were 46% , 75% and ranged 0 - 230 ng/L, 0 - 72.3 ng/L respectively. Several PFCs were showed same level of the detection

rate of PFOS, PFHxA was 52%, PFHpA was 43%, PFNA was 40%. The detection rate of PFHpS, PFDS, PFDA, PFTrDA were low. Max concentration of PFHxS was high and same level of PFOS. These concentrations of PFCs were higher than the Tama river main stream in the suburb area of Tokyo⁵⁾.

The totaled concentrations of PFCs were more than 100 ng/L in some samples, as shown in figure-2. Most samples indicate in figure-2 were collected in suburb area of Tokyo. These result introduced that large pollutant sources of PFCs were exists in this area. The compositions of PFCs were similar in No.31, No.36 and No.44. However, these samples were collected from faraway cities in the suburb area, there were the own sources of these groundwater samples and each pollutions may have common points.

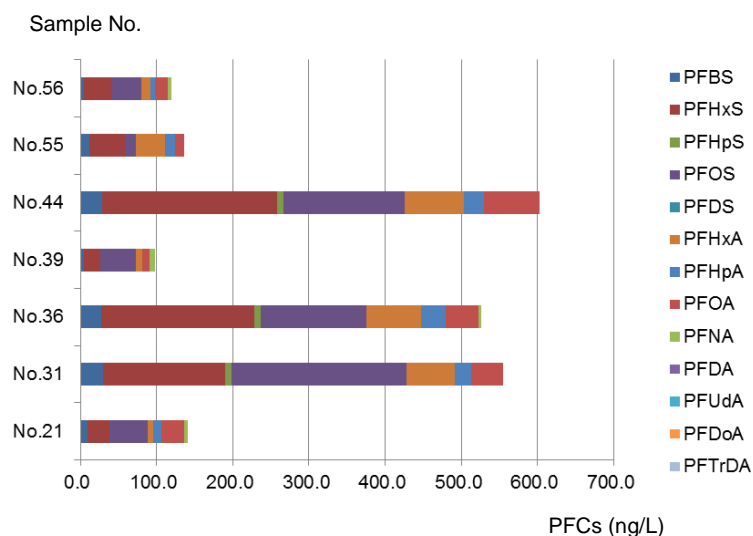


Fig.2 Compositions of PFCs in groundwater samples

Acknowledgments

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References

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Table 3 Concentration of PFCs in groundwater

Sample No.	Concentration(ng/L)												
	PFBS	PFHxS	PFHpS	PFOS	PFDS	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTrDA
No.1	N.D.	5.8	N.D.	6.1	N.D.	(2.5)	(2.1)	8.8	2.4	N.D.	N.D.	N.D.	N.D.
No.2	(1.5)	(4.4)	N.D.	(2.0)	N.D.	(1.4)	(1.7)	6.0	N.D.	N.D.	N.D.	N.D.	N.D.
No.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
No.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.0)	N.D.	N.D.	(1.3)	(1.6)
No.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.0)	N.D.	N.D.	N.D.	N.D.	N.D.
No.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
No.7	3.9	N.D.	N.D.	3.5	N.D.	(1.8)	(2.1)	6.6	13	N.D.	N.D.	N.D.	N.D.
No.8	(1.8)	(3.9)	N.D.	(2.9)	N.D.	(1.9)	(1.7)	5.5	N.D.	N.D.	N.D.	N.D.	N.D.
No.9	(2.4)	N.D.	N.D.	(2.7)	N.D.	(1.7)	(2.0)	2.0	(1.6)	N.D.	N.D.	N.D.	N.D.
No.10	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.1)	N.D.	N.D.	N.D.	N.D.	N.D.
No.11	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.2)	N.D.	N.D.	N.D.	N.D.
No.12	N.D.	N.D.	N.D.	(2.9)	N.D.	(1.5)	N.D.	(1.1)	(1.8)	N.D.	N.D.	N.D.	N.D.
No.13	4.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.7)	N.D.	N.D.	N.D.	(1.5)	N.D.
No.14	N.D.	7.2	N.D.	(1.8)	N.D.	(2.2)	N.D.	5.5	(1.3)	N.D.	N.D.	N.D.	N.D.
No.15	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.2	N.D.	N.D.	N.D.	N.D.	N.D.
No.16	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
No.17	(1.4)	(3.7)	N.D.	(2.4)	N.D.	(1.5)	N.D.	5.0	N.D.	N.D.	N.D.	(1.3)	N.D.
No.18	N.D.	N.D.	5.9	3.9	(2.4)	(3.1)	4.2	7.2	(1.9)	N.D.	N.D.	(1.3)	7.9
No.19	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	3.0	N.D.	N.D.	N.D.	N.D.	2.9
No.20	(1.3)	(2.2)	N.D.	N.D.	N.D.	8.1	22	36	N.D.	N.D.	N.D.	(1.4)	N.D.
No.21	9.3	29	(2.7)	51	N.D.	7.1	10	30	4.6	N.D.	N.D.	N.D.	(1.5)
No.22	(1.7)	5.8	N.D.	9.0	N.D.	3.4	(2.5)	6.2	3.2	N.D.	N.D.	N.D.	N.D.
No.23	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.9	N.D.	N.D.	N.D.	N.D.	N.D.
No.24	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
No.25	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
No.26	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.2)	N.D.	N.D.	(1.5)	(1.4)	N.D.
No.27	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
No.28	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.1)	N.D.	N.D.	(1.4)	(1.6)	N.D.
No.29	(2.1)	N.D.	N.D.	N.D.	N.D.	(2.1)	N.D.	(0.7)	N.D.	N.D.	(1.7)	(1.7)	N.D.
No.30	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.6	N.D.	N.D.	N.D.	N.D.	N.D.
No.31	30	160	8.8	230	N.D.	63	21	42	N.D.	N.D.	N.D.	N.D.	N.D.
No.32	N.D.	(2.6)	N.D.	3.5	N.D.	(1.7)	(2.4)	5.8	5.4	N.D.	N.D.	N.D.	N.D.
No.33	N.D.	14	N.D.	27	N.D.	5.6	(3.1)	8.5	4.4	N.D.	N.D.	(3.1)	N.D.
No.34	(1.9)	6.5	N.D.	15	N.D.	4.2	(2.4)	7.9	7.7	N.D.	N.D.	N.D.	N.D.
No.35	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.7)	(1.8)	N.D.
No.36	28	200	8.2	140	N.D.	72	32	43	4.0	N.D.	N.D.	N.D.	N.D.
No.37	(1.3)	(2.5)	N.D.	8.7	N.D.	(2.5)	(2.5)	6.4	14	N.D.	N.D.	3.9	N.D.
No.38	N.D.	(3.1)	N.D.	N.D.	N.D.	(2.2)	N.D.	2.2	N.D.	N.D.	N.D.	3.9	N.D.
No.39	4.3	22	N.D.	46	N.D.	8.4	(2.1)	9.5	7.3	N.D.	(2.1)	(1.7)	N.D.
No.40	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
No.41	N.D.	N.D.	N.D.	5.4	N.D.	(2.8)	(1.5)	4.8	(2.4)	N.D.	N.D.	N.D.	N.D.
No.42	(1.7)	N.D.	N.D.	(1.5)	N.D.	N.D.	N.D.	1.9	N.D.	N.D.	N.D.	N.D.	N.D.
No.43	3.8	21	N.D.	23	N.D.	7.7	5.3	12	7.3	(1.2)	3.3	5.5	N.D.
No.44	28	230	7.9	160	N.D.	77	27	73	(1.9)	N.D.	N.D.	N.D.	N.D.
No.45	(1.3)	N.D.	N.D.	6.1	N.D.	5.4	5.6	13	5.9	N.D.	N.D.	(3.0)	N.D.
No.46	5.0	22	N.D.	30	N.D.	8.2	(2.9)	8.5	12	N.D.	N.D.	N.D.	N.D.
No.47	N.D.	N.D.	N.D.	N.D.	N.D.	(1.8)	(1.3)	3.2	N.D.	N.D.	N.D.	N.D.	N.D.
No.48	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
No.49	N.D.	N.D.	N.D.	7.4	N.D.	(2.8)	(2.4)	5.9	5.5	N.D.	N.D.	N.D.	N.D.
No.50	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.2	N.D.	N.D.	N.D.	N.D.	N.D.
No.51	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
No.52	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.0)	N.D.	N.D.	N.D.	N.D.	N.D.
No.53	(1.7)	N.D.	N.D.	4.4	N.D.	(2.6)	(3.1)	8.7	(1.7)	N.D.	N.D.	N.D.	N.D.
No.54	(2.1)	N.D.	N.D.	3.8	N.D.	(1.5)	(1.7)	5.4	(1.9)	N.D.	(2.8)	5.3	N.D.
No.55	11	47	(2.2)	15	N.D.	38	13	12	N.D.	N.D.	N.D.	N.D.	N.D.
No.56	5.1	35	N.D.	40	N.D.	12	6.2	17	4.6	N.D.	N.D.	N.D.	(1.2)
No.57	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.0)	N.D.	N.D.	N.D.	N.D.	N.D.
No.58	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
No.59	N.D.	(3.2)	N.D.	N.D.	N.D.	(1.4)	N.D.	67	N.D.	N.D.	3.4	6.4	N.D.
No.60	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.3)	(1.3)	N.D.
No.61	N.D.	N.D.	N.D.	3.5	N.D.	(2.1)	(2.4)	7.1	5.1	N.D.	N.D.	5.8	N.D.
No.62	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.5	N.D.	N.D.	4.2	6.7	N.D.
No.63	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.1)	N.D.	N.D.	N.D.	N.D.	N.D.
No.64	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.6)	(1.6)	N.D.
No.65	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(1.8)	(1.6)	N.D.
Detection rate	37%	34%	9%	46%	2%	52%	43%	75%	40%	2%	18%	34%	8%
Max	29.7	230	8.8	230	0.0	77.4	31.7	72.7	14.0	0.0	4.2	6.7	7.9

N.D. : not detected, () : Below the limit of quantitation