FACT-FINDING SURVEY ON PERFLUORINATED COMPOUNDS IN WASTEWATERS

Takahashi A[1],Nishino T[1], Fujinami H[1], Sasaki Y[2], Takazawa Y[2], Shibata Y[2], Takashima Y[3], Omata T[3], Kitano M[3]
[1]Tokyo Metropolitan Research Institute for Environmental Protection, 1-7-5 Shinsuna, Koto-ku, Tokyo 136-0075, Japan; [2]National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-8506 Japan; [3] Meiji University, 1-1 Kandasurugadai, Chiyoda-ku, Tokyo, 101-8301, Japan

Abstract
Perfluorooctane sulfonate (PFOS) was detected at a higher concentration in the Tama River. In this study, wastewater samples from many industries were analyzed to identify the emission source of perfluorinated compounds (PFCs). We analyzed 14 PFCs and 9 were detected: PFHxA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrA PFHxS and PFOS. PFCs were detected at high concentrations in wastewaters from MFR Electronic Components, Medical Laboratories, Carpet & Upholstery Cleaning. PFUdA and PFTrA were highly concentrated than PFOA, which are more widely and frequently used in such industries. Many PFCs include PFOS and PFOA were discharged from many category of industries. Some category of industries were discharged many PFCs together, for example Medical Laboratories, MFR Electrical Equipment and Chemical industry.

Introduction
In May 2009, perfluorooctane sulfonate (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F) were listed as Annex B persistent organic pollutants (POPs) under the Stockholm Convention [1)]. Regarding perfluorooctanoic acid (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 chemicals[2)]. In Japan, the perfluorinated compounds (PFCs) surveillance at public water areas, PFOS and PFOA were frequently detected in river water[3)]. These PFCs were detected in final discharge from Wastewater Treatment Plants (WWTPs) in Japan[4)]. WWTPs receive PFCs from industrial wastewaters, but In Japan, many WWTPs use biological treatment process and PFCs are not completely removed by the treatment processes and are ultimately discharged into surface waters[4)].

It is considered that understanding emission sources is necessary for decreasing PFCs discharges. This paper focuses on the middle reaches of the Tama River in Tokyo because it is one of the most urbanized rivers in Japan as shown in Figure-1. The population on its drainage basin is 2.1 million and sewerage systems serve 1.8 million people and WWTPs effluent accounts for a maximum of 30% of the water in the river.
PFOS was detected at the higher concentration in the Tama river than the average concentration of nationwide survey.

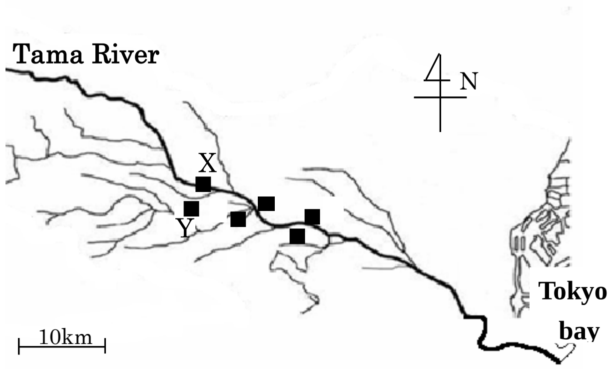

Fig. 1 Outline of the Tama River (■ :WWTPs)

Material and Methods

Samples

Wastewater samples were collected in the treatment district of X WWTPs and Y WWTPs and stored in 250 mL polypropylene bottles. Sampling points shows in fig. 2.

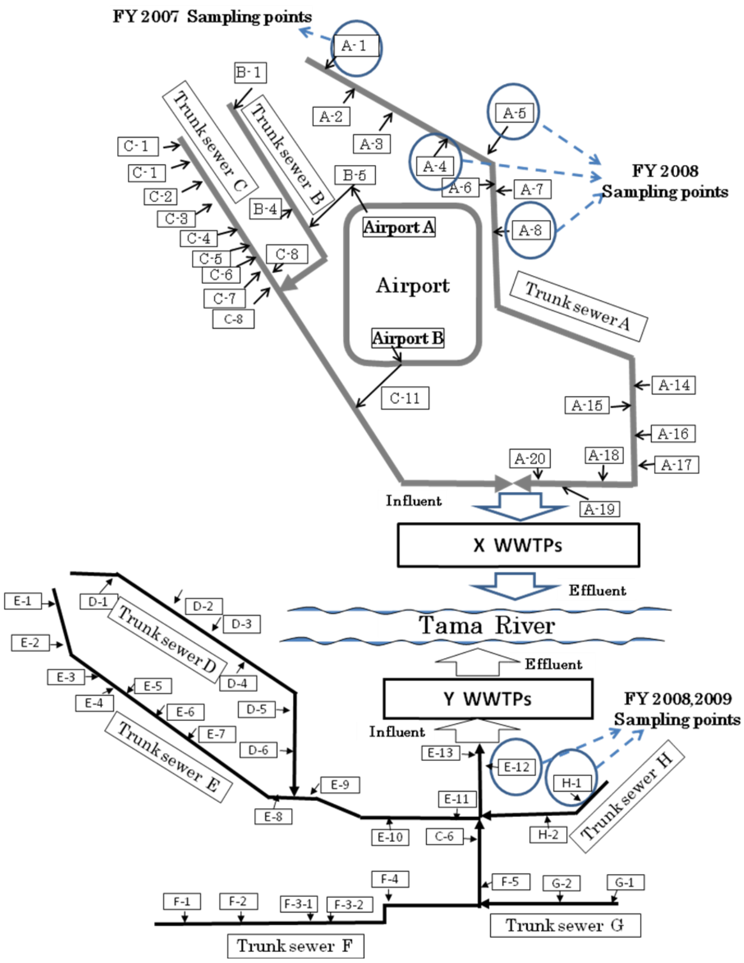

Fig.2 Sampling points of wastewater

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. (In FY 2007, We used standard mixture containing PFOS , PFOA, PFHxS and these mass-labeled compounds.)

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)

Analysis of samples

Water samples were collected and stored in 250 mL polypropylene bottles. 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 5mL of 1% ammonium hydroxide in methanol. After elution, it was concentrated by N_2 purge to 1 mL, adjusted to 2 mL with 50% methanol in H_2O, and filtered through a 0.2 µm nylon membrane filter. The final sample was analyzed using LC/MS/MS (PremierXE; Waters Corp., Milford USA).

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

Table 2 shows the results analysis of PFCs in wastewaters flowing into X WWTPs (trunk sewer A) sampled in FY 2007. PFOS was detected at 10 samples ranged 6 to 58,000 ng/L and the MFR Electronic Components was highly concentrated. And PFOS of MFR Transportation Equipment A and Airport B were also concentrated. PFOA was detected at 16 samples ranged 6 to 27 ng/L.

Table 3 shows the results analysis of PFCs in wastewaters flowing into X WWTPs (trunk sewer A) sampled in FY 2008. In these samples, only five were detected: PFOA, PFOS, PFHxA and PFUdA and PFNA. Other PFCs were below the detection limits.

PFNA were detected at 280 ng/L concentration in the wastewater from MFR Transportation Equipment B and at 140 ng/L concentration in the wastewater from MFR Fabricated Nonferrous Metal Products.

PFNA were higher than PFOA in these wastewaters of this area.

Table 2 Concetration of PFCs in wastewaters flowing into X WWTPs (FY 2007)

Category of Industry	Trunk Sewer	Sampling Date	Chemicals		
			PFOS	PFOA	PFHxS
Research Laboretrory A	A-1	2007/Oct.	N.D.	N.D.	N.D.
Research Laboretrory B	A-1	2007/Oct.	N.D.	N.D.	N.D.
MFR Electrical Equipment A	A-1	2007/Oct.	7	6	N.D.
Communications Equipment	A-1	2007/Oct.	6	ND	N.D.
MFR Transportation Equipment A	A-1	2007/Oct.	240	6	N.D.
MFR Electrical Equipment B	A-1	2007/Oct.	14	10	N.D.
MFR Fabricated Metal Products A	A-1	2007/Oct.	23	6	N.D.
Food Preparetions A	A-1	2007/Oct.	N.D.	ND	N.D.
Food Preparetions B	A-1	2007/Oct.	N.D.	6	N.D.
MFR Electronic Components A	A-1	2007/Oct.	N.D.	6	N.D.
MFR Electronic Components B	A-1	2007/Oct.	N.D.	7	N.D.
MFR Electronic Components C	A-1	2007/Oct.	36	16	N.D.
MFR Electronic Components D	A-1	2007/Oct.	58,000	22	18
Hospital A	A-1	2007/Oct.	N.D.	6	N.D.
Hospital B	A-1	2007/Oct.	N.D.	7	N.D.
Hospital C	A-1	2007/Oct.	N.D.	6	N.D.
Refuse systems	A-1	2007/Oct.	N.D.	27	N.D.
MFR Electronic Components E	B-1	2007/Oct.	60	7	50
MFR Electrical Equipment C	B-1	2007/Oct.	N.D.	N.D.	N.D.
Chemical industry	B-1	2007/Oct.	N.D.	N.D.	N.D.
Airport A	B-5	2007/Nov.	23～83	7	N.D.
Airport B	C-11	2007/Nov.	67～410	9～10	8～61

MFR : Manufacturing ng/L N.D. : Not detected

Table 3 Concetration of PFCs in wastewaters flowing into X WWTPs (FY 2008)

Category of Industry	Trunk Sewer	Sampling Date	Chemicals								
			PFHxA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTrA	PFHxS	PFOS
MFR Fabricated Nonferrous Metal Products	A-4	2009/Jan.	19	N.D.	140	N.D.	10	N.D.	N.D.	N.D.	240
Animal & Marine Fats & Oils	A-5	2008/Sep.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
MFR Fabricated Metal Products B	A-5	2008/Sep.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	10
MFR Transportation Equipment B	A-8	2008/Sep.	N.D.	7.9	280	N.D.	30	N.D.	N.D.	N.D.	22

MFR : Manufacturing ng/L N.D. : Not detected

Table 4 shows the results analysis of PFCs in wastewaters flowing into Y WWTPs (trunk sewer E and H) sampled in FY 2008-2009. In these samples, 9 PFCs were detected. PFNA were detected at 220-6,200 ng/L concentration in the wastewater from Medical Laboratories A and at 180-3,100 ng/L concentration in the wastewater from Medical Laboratories B. PFUdA and PFTrA concentrations of these Medical Laboratories were also high concentrated. PFNA was detected at 320-820 ng/L concentration in the wastewater from Carpet & Upholstery Cleaning, too. Many PFCs include PFOS and PFOA were discharged from many category of industries. Some category of industries were discharged many PFCs together, for example Medical Laboratories, MFR Electrical Equipment and Chemical industry.

Table 4 Concetration of PFCs in wastewaters flowing into Y WWTPs (FY 2008, 2009)

Category of Industry	Trunk Sewer	Sampling Date	Chemicals								
			PFHxA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTrA	PFHxS	PFOS
Medical Laboratories A	E-12	2009/Mar.	N.D.	8.7	220	7.2	52	13	67	70	12
		2009/Sep.	43	120	6,200	21	740	16	190	70	20
		2009/Dec.	5.4	14	1,400	9.3	790	10	320	32	14
Medical Laboratories B	E-12	2009/Mar.	5.9	34	270	12	120	8.3	95	N.D.	88
		2009/Sep.	9.1	17	180	5.2	180	14	34	N.D.	20
		2009/Dec.	11	50	3,100	16	1,100	14	200	7.9	25
Medical Laboratories C	E-12	2009/Mar.	N.D.	3.3	16	1.5	13	7.5	N.D.	N.D.	1.5
		2009/Sep.	2.1	3.6	14	N.D.	5.4	N.D.	N.D.	N.D.	12
		2009/Dec.	2.1	3.9	48	3.1	15	3.0	N.D.	3.0	3.6
Research Laboretrory A	E-12	2009/Mar.	—	—	—	—	—	—	—	—	—
		2009/Sep.	1.3	2.3	4.3	0.1	3.5	1.2	1.1	N.D.	1.2
		2009/Dec.	1.3	3.0	3.4	2.2	3.4	4.2	0.3	N.D.	2.3
MFR Electrical Equipment B	E-12	2009/Mar.	8.2	6.2	6.3	1.8	5.3	N.D.	N.D.	4.7	7.1
		2009/Sep.	8.5	16	190	5.4	24	3.2	1.7	N.D.	7.1
		2009/Dec.	7.0	12	130	4.7	38	5.4	7.0	17	8.8
MFR Electrical Equipment B	E-12	2009/Mar.	5.9	10	17	1.6	3.0	N.D.	N.D.	12	5.0
		2009/Sep.	1.3	3.0	4.8	1.8	N.D.	1.4	N.D.	N.D.	1.5
		2009/Dec.	3.5	8.6	12	4.3	4.7	5.7	N.D.	25	9.2
Carpet & Upholstery Cleaning	H-1	2009/Mar.	N.D.	30	320	6.5	5.0	N.D.	N.D.	3.2	2.1
		2009/Sep.	N.D.	N.D.	820	84	N.D.	N.D.	97	N.D.	N.D.
		2009/Dec.	7.2	30	440	2.5	10	4.3	N.D.	15	11
Chemical industry	H-1	2009/Mar.	N.D.	12	36	1.4	5.9	N.D.	N.D.	12	8.0
		2009/Sep.	6.4	16	31	N.D.	N.D.	2.9	2.1	N.D.	N.D.
		2009/Dec.	7.9	20	54	2.5	6.4	5.1	N.D.	49	18

MFR : Manufacturing ng/L N.D. : Not detected

Acknowledgments

This work was supported by Environment Research and Technology Development Funds of the Ministry of the Environment, Japan (M-06)

References

1) http://chm.pops.int/

2) http://www.epa.gov/opptintr/pfoa/pubs/stewardship/index.html

3)Takazawa Y. et al., (2004). Perfluorooctane sulfonate found in river water from the Tokyo Metropolitan area, *Proc. China–Japan Joint Symposium on Environmental Chemistry*, pp365–366.

4)Nisino T. et al., (2009). Analyzes of Pefluorinated compounds in sewage and drainage, Organohalogen Compound s, 71,1640-1643