Contaminated revelation of PFCs in a water regime in Tokyo

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Abstract

PFCs have on superior characteristics of heat resistance and chemical resistance, and they are often used for industrial applications. Thereafter, they are mainly drained as factory effluent into the environment. Because PFCs drained into the environment have high water solubility, they exist in hydrosphere in the environment. We analyzed PFCs in Tokyo bay and theTama river in Tokyo using LC/MS/MS to investigate the actual situation of these environmental pollutants. The measured chemicals were 13: PFBS, PFHxS, PFHxA, PFHpS, PFHpA, PFOS, PFOA, PFNA, PFDS, PFDA, PFUdA, PFDoA, PFTrDA. In the depth of the Tokyo bay PFHpS, PFHxA, PFHxS, PFOA, PFOS, PFNA, and PFDA were detected. And in the Tama river PFOA, PFOS, and PFNA were detected. Comparison of concentrations of PFCs in the Tama River in December 2008 to those in July 2008 revealed decreased concentrations of PFOS. No significant differences were found in the concentrations of PFOA between the two months.

Introduction

Toxic substances such as dioxins, PCBs, and DDT are persistent in the environment. And, they are accumulated in biota, move a long range on the earth too. Finally, they are toxic to wild animals. Chemical substances that have such properties are called Persistent Organic Pollutants (POPs), which are regulated globally by the POPs treaty. PFOS is a representative material of PFCs. It is added to be regulated substances in 2009.The strong carbon-fluorine bond in PFOS imparts superior heat resistance and chemical resistance properties; it is a stable compound. Consequently, it is used in various applications as a surface preparation agent and water repellent agent. Unfortunately, because of its stability, it is persistent in the environment. It is reportedly found in humans and wild animals years after exposure. Because PFCs have high water solubility, they are mainly found in water environment. For that reason, we measured PFCs in a water regime inside Tokyo, and investigated their actual environmental pollution.

Materials and Method

Samples

We collected seawater at two sampling points (St. 1, 2) of Tokyo Bay ,where Tokyo metropolitan government conducts water surveys of public water areas regularly, in October 2008. We collected seawater at sampling points (St. 3, 5, 6, 8, 12, 18, 23, 24, 25, 31) of Tokyo Bay in February 2009. Additionally, we collected river water at four spots of Nagata Bridge, Hino Bridge, Sekito Bridge, and Tamagawara Bridge on the middle stream of the Tama River.

Standards

The standard compounds used for this study are standard mixture solutions produced by Wellington Laboratories Inc.(Ontario,Canada). Standard mixture solution contains nine mass-labeled perfluorocompounds (MPFAC-MXA: each element 2 μg/mL in methanol solution). The MPFAC-MXA was diluted to 200 ng/mL with

methanol and used as an internal standard mixture. Table 1 presents a list of the standard mixtures and contained compounds.

Table 1 List of Compounds in standard solution.

Standard	Compounds in standard solution
MPFAC-MXA (labeled mixture)	$^{13}C_4$-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

Analyses of samples

The seawater and river water samples were collected and stored in 1-liter polypropylene bottles. The water sample was filtered using 0.4 μm glass fiber filtration paper (GB-140; Toyo Roshi Kaisha Ltd., Tokyo, Japan). Before solid phase extraction, 100 μL of internal standard mixture was added to the filtrate. For use as a solid phase extraction column, a weak anion exchange cartridge column (OASIS-WAX; Waters Corp., Milford USA) was purchased. This cartridge was preconditioned, using 5 mL of methanol, and 10 mL of ultrapure water. The PFCs were extracted on solid phase at the flow rate of 5 mL/min. After extraction, an OASIS-WAX cartridge column was eluted using 5 mL of 1% ammonium hydroxide in methanol. After elution, it was concentrated to 1 mL under N_2 stream, and adjusted to 2 mL with 50% methanol in H_2O and filtered again through a 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

LC/MS/MS(Premier XE, Waters) equipped with L-column 2 (φ2.1 mm × 150 mm made by CERI, particle size 3 μm).was used. Injection volume is 10 micro litters and column temperature is 40 degree Celsius. Regarding the ionization method for ESI (negative mode), the measurement mode, MRM, the ion source temperature was 120°C and the de-solvent temperature was 350°C. The measured materials were PFBS, PFHxS, PFHpS, PFHpA, PFHxA, PFHxS, PFNA, PFDS, PFDA, PFUdA, PFDoA, PFTrD. As a eluent for the LC, 10 mM acetate ammonium and acetonitrile were used.

Results and Discussion

The limit of quantification shows in Table 2. Sampling points in the Tokyo bay shows in Fig. 1 , The result shows in Table 3. Detected substances were PFHpS, PFHxA, PFHxS, PFOA, PFOS, PFNA, and PFDA. Although other PFCs were not detected, the existence of PFCs was confirmed in the depth of Tokyo Bay.

Table 2 limit of quantitation of PFCs

the limit of quantitation / ng L^{-1}								
PFHxA	PFHpA	PFOA	PFNA	PFUdA	PFDA	PFBS	PFHxS	PFOS
2.0	2.4	1.3	1.8	5.0	1.1	1.4	2.1	1.0

Table 3 Concentration of PFCs in Tokyo Bay.

Sampling points	Sampling times	Concentration / ng L^{-1}								
		PFHxA	PFHpA	PFOA	PFNA	PFUdA	PFDA	PFBS	PFHxS	PFOS
St 1	October 2008	N.D	—	9.0	8.4	—	—	—	4.5	6.3
St 2	October 2008	2.2	—	6.8	17	—	—	—	4.2	16
St 3	February 2009	N.D	(1.1)	5.5	5.3	N.D	(0.4)	N.D	(1.2)	3.4
St 5	February 2009	7.7	N.D	4.6	13	N.D	(0.5)	N.D	2.6	8.0
St 6	February 2009	6.4	N.D	6.4	4.0	N.D	(0.4)	N.D	(1.1)	3.2
St 8	February 2009	N.D	N.D	5.2	5.0	N.D	(0.6)	N.D	(1.3)	3.1
St 12	February 2009	6.2	N.D	6.0	7.6	N.D	(0.7)	N.D	(1.5)	4.8
St 18	February 2009	(1.4)	N.D	4.4	5.9	N.D	(0.5)	N.D	(1.1)	6.0
St 23	February 2009	N.D	(1.3)	7.2	12	N.D	(0.9)	N.D	2.2	8.6
St 24	February 2009	3.4	(1.1)	6.2	8.2	N.D	(0.5)	N.D	(1.8)	6.0
St 25	February 2009	N.D	N.D	5.4	4.8	N.D	(0.5)	N.D	(1.0)	3.2
St 31	February 2009	6.7	(1.3)	6.4	7.5	N.D	(0.6)	N.D	2.9	6.8

—:Unanalyzed N.D.:Not Detected ( ):Below the limit of quantitation

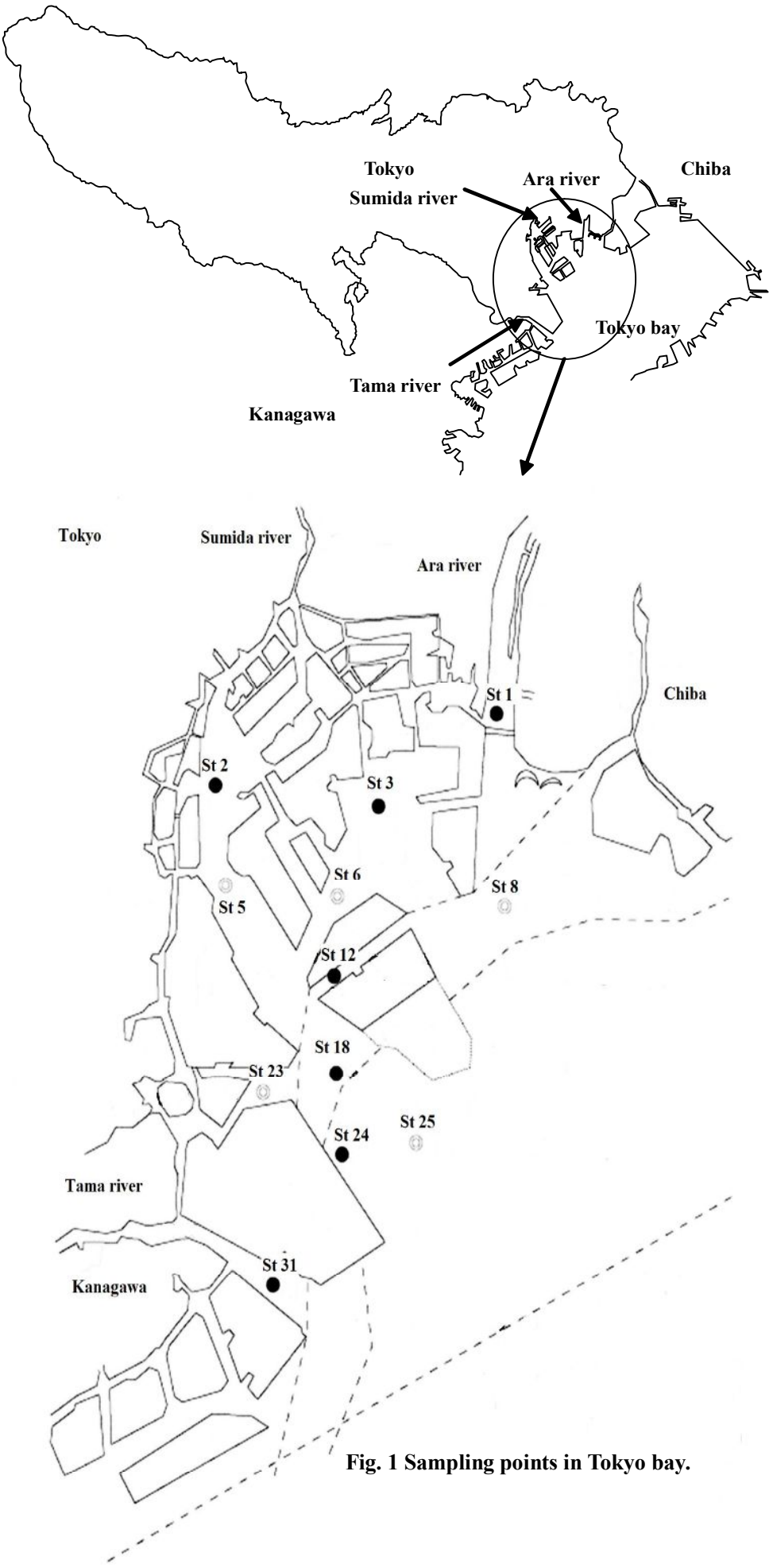

Fig. 1 Sampling points in Tokyo bay.

Sampling points in the Tama River shows in Fig. 2 , the result shows in Table 4. PFOA, PFOS, and PFNA were detected and, other PFCs were not. Results indicate that the sources of PFCs pollution may locate in the middle stream of the river. The number of PFCs detected in the Tama River were less than those found in Tokyo Bay. Therefore, it is necessary to investigate the pollution at the sampling points of the upper stream in other rivers, e.g., the Arakawa River, Sumida River, to specify Tokyo Bay's PFC contamination source.

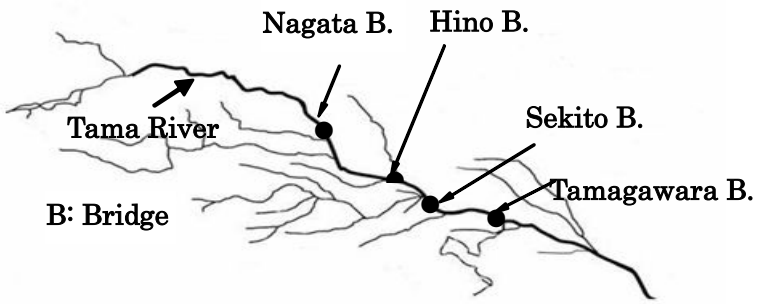

Fig. 2 Sampling points in the Tama River.

Table 4 Concentration of PFCs in Tama River.

Sample name	July 2008			December 2008		
	Concentration / ng L^{-1}			Concentration / ng L^{-1}		
	PFOA	PFOS	PFNA	PFOA	PFOS	PFNA
Nagata B.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Hino B.	6.0	31	N.D.	8.5	11	11
Sekito B.	9.5	81	6.4	8.8	15	15
Tamagawara B.	17	81	7.1	9.2	17	14

N.D.: Not detected

Comparison of concentrations of PFCs in the Tama River in December 2008 to those in July 2008 revealed decreased concentrations of PFOS. Probably, managers of factories using PFOS feared the addition of PFOS to the regulated substances under the POPs treaty, and refrained from using them. While the concentration of PFOA was rather constant. As PFOS and PFOA are used in the different industries, this may be the reason of the different concentration change. The US-EPA devised a management program that reduces PFOA discharges. We intend to investigate the annual change in the concentrations of these PFCs.

Acknowledgements

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