Biennial survey of perfluoroalkyl and polyfluoroalkyl substances in river water from Saitama Prefecture, Japan during 2009-2017

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Introduction:
Perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been widely used for commercial and industrial applications such as surfactants, lubricants, paper and textile coatings, and fire-fighting foams. PFASs mainly consist of perfluoroalkane sulfonic acids (PFSAs) and the precursor group, including chemicals such as perfluorooctane sulfonic acid (PFOS), and perfluoroalkyl carboxylic acids (PFCAs) and the precursor group, including chemicals such as perfluorooctanoic acid (PFOA). The precursors are derivatives of PFSAs or PFCAs, also used for commercial and industrial applications, and are thought to be broken down to PFSAs or PFCAs in the environment[1-4]. Many researchers have reported a global distribution of PFOS and PFOA in surface water, groundwater, sediment, and biota[5,6]. PFOS and PFOA are persistent accumulating in the environment, and thus affecting organisms[7-9]. PFOS has been determined to be a persistent organic pollutant (POP) under the Stockholm Convention in 2009, and was restricted its use. In 2015, the Stockholm Convention POP Review Committee suggested that PFOA may be identified as a POP in the future. Recently, it is thought that transition to substitute chemicals has been promoted by worldwide reduction efforts for PFOS and PFOA. In this study, we conducted a biennial survey of PFASs in river water to elucidate the concentration changes under the regulation on PFOS and PFOA.

Materials and methods:
The biennial survey was conducted in April, 2009, 2011, 2013, 2015, and 2017. Thirty eight locations from 35 rivers in Saitama Prefecture, located boundary on the north of Metropolitan Tokyo were selected as monitoring station. Approximately 500 mL of surface water was collected into a polypropylene centrifugal bottle using a stainless steel bucket.
Thirty eight target PFASs in this study were shown in Table 1. Five PFSAs were perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), perfluoroheptane sulfonic acid (PFHpS), PFOS, and perfluorodecane sulfonic acid (PFDS). Ten precursors of PFOS were perfluorooctane sulfinic acid (PFOSi), perfluorooctane sulfonamide (FOSA), N-methyl perfluorooctane sulfonamide (N-MeFOSA), N-ethyl perfluorooctane sulfonamide (N-EtFOSA), N,N-dimethyl perfluorooctane sulfonamide (N,N-Me2FOSA), perfluorooctane sulfonamidoacetic acid (FOSAA), N-methyl perfluorooctane sulfonamidoacetic acid (N-MeFOSAA), N-ethyl perfluorooctane sulfonamidoacetic acid (N-EtFOSAA), N-Methyl perfluorooctane sulfonamidoethanol (N-MeFOSE), and N-Ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE). Six PFCAs were perfluoro pentnoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDA). Seventeen precursors of PFCAs were 6:2 fluorotelomer unsaturated carboxylic acid (6:2FTUCA), 6:2 fluorotelomer carboxylic acid (6:2FTCA), 8:2 fluorotelomer unsaturated carboxylic acid (8:2FTUCA), 8:2 fluorotelomer carboxylic acid (8:2FTCA), 10:2 fluorotelomer unsaturated carboxylic acid (10:2FTUCA), 10:2 fluorotelomer carboxylic acid (10:2FTCA), 3:3 saturated acid (3:3FTCA), 5:3 saturated acid (5:3FTCA), 7:3 saturated acid (7:3FTCA), 5:2 secondary fluorotelomer alcohol (5:2sFTOH), 7:2 secondary fluorotelomer alcohol (7:2sFTOH), 6:2 fluorotelomer alcohol (6:2FTOH), 8:2 fluorotelomer alcohol (8:2FTOH), 10:2 fluorotelomer alcohol (10:2FTOH), 4:2 fluorotelomer sulfonic acid (4:2FTS), 6:2 fluorotelomer sulfonic acid (6:2FTS), and 8:2 fluorotelomer sulfonic acid (8:2FTS).
The extraction of N,N-Me2FOSA, 5:2sFTOH, 7:2sFTOH, 6:2FTOH, 8:2FTOH, and 10:2FTOH in the water sample was according to purge trap extraction method[10]. Briefly, 400 mL of water sample was gently poured into a 1000-mL gas washing bottle. An internal standard ($^{13}C_2,d_2$-6:2FTOH, $^{13}C_2,d_2$-8:2FTOH, and $^{13}C_2,d_2$-10:2FTOH) and sodium chloride were added into the sample, and the bottle was placed in an ultrasonic water bath at 40°C. Indoor air through gas filters (activated carbon) was aerated to the bottle using a vacuum pump, then extracted target chemicals from water phase were trapped on an SPE cartridge (InertSep RP-1 mini). The target chemicals were eluted with 3 mL of dichloromethane, and the eluate was concentrated to 0.5 mL under a

gentle stream of N_2 gas at 30°C. These chemicals were measured using GC/MS (Agilent 6890 / JEOL GCmateII or ThermoFisher Trace GC / ISQ).

Table 1: Concentration ranges of PFASs in river water

ng/L

Classification	Symbol	Formula	Apr. 2009	Apr. 2011	Apr. 2013	Apr. 2015	Apr. 2017
Perfluoroalkane sulfonic acids (PFSAs) and the precursors	PFBS	$C_4F_9SO_3H$	NA*	NA	NA	<0.6-3.0	<0.6-16
	PFHxS	$C_6F_{13}SO_3H$	NA	NA	NA	<0.5-9.3	<0.5-8.7
	PFHpS	$C_7F_{15}SO_3H$	NA	NA	NA	<0.4-0.6	<0.4-0.6
	PFOS	$C_8F_{17}SO_3H$	<0.8-110	<0.5-79	<0.9-29	<0.5-26	<0.5-61
	PFDS	$C_{10}F_{21}SO_3H$	NA	NA	NA	<0.2	<0.2-0.2
	PFOSi	$C_8F_{17}SO_2H$	<0.2-1.7	<0.2-1.0	<0.2-0.3	<0.4	<0.4
	FOSA	$C_8F_{17}SO_2NH_2$	0.5-1.6	<0.4-0.9	<0.1-1.9	<0.8	<0.8-0.8
	N-MeFOSA	$C_8F_{17}SO_2NH(CH_3)$	<0.7-8.0	<0.7-1.8	<0.5	<0.6	<0.6
	N-EtFOSA	$C_8F_{17}SO_2NH(C_2H_5)$	<0.5	<0.5	<0.3	<0.7	<0.7
	N,N-Me2FOSA	$C_8F_{17}SO_2N(CH_3)_2$	<0.3	<0.4	<0.4	<0.4	NA
	FOSAA	$C_8F_{17}SO_2NH(CH_2COOH)$	<0.4	<0.4	<0.4	<0.8	<0.8
	N-MeFOSAA	$C_8F_{17}SO_2N(CH_3)(CH_2COOH)$	<0.3-0.8	<0.3-0.6	<0.4-1.2	<1	<1
	N-EtFOSAA	$C_8F_{17}SO_2N(C_2H_5)(CH_2COOH)$	<0.1-0.7	<0.1-1.1	<0.3-0.4	<0.7	<0.7
	N-MeFOSE	$C_8F_{17}SO_2N(CH_3)(C_2H_4OH)$	<0.7	<0.7-1.5	<0.4	<0.6	<0.6
	N-EtFOSE	$C_8F_{17}SO_2N(C_2H_5)(C_2H_4OH)$	<0.6	<0.6	<0.7	<0.5	<0.5
Perfluoroalkyl carboxylic acids (PFCAs) and the precursors	PFPeA	C_4F_9COOH	NA	NA	NA	<0.2-6.0	<0.2-4.3
	PFHxA	$C_5F_{11}COOH$	NA	NA	NA	<0.3-13	<0.3-12
	PFHpA	$C_6F_{13}COOH$	NA	NA	NA	<0.3-5.5	<0.3-6.5
	PFOA	$C_7F_{15}COOH$	<0.6-42	<0.6-86	<0.4-1300	<0.4-19	<0.4-15
	PFNA	$C_8F_{17}COOH$	NA	NA	NA	<0.6-11	<0.6-11
	PFDA	$C_9F_{19}COOH$	NA	NA	NA	<0.4-1.1	<0.4-1.6
	6:2FTUCA	$C_5F_{11}CFCHCOOH$	NA	NA	NA	NA	<0.3-1.0
	6:2FTCA	$C_6F_{13}CH_2COOH$	NA	NA	NA	NA	<7
	8:2FTUCA	$C_7F_{15}CFCHCOOH$	<3	<3	<0.5	<0.7	<0.7-1.5
	8:2FTCA	$C_8F_{17}CH_2COOH$	<2-2	<2	<3	<5	<5
	10:2FTUCA	$C_9F_{19}CFCHCOOH$	NA	NA	NA	NA	<0.3
	10:2FTCA	$C_{10}F_{21}CH_2COOH$	NA	NA	NA	NA	<3
	3:3FTCA	$C_3F_7CH_2CH_2COOH$	NA	NA	NA	<0.1	<0.1-0.1
	5:3FTCA	$C_5F_{11}CH_2CH_2COOH$	NA	NA	NA	<0.3-3.9	<0.3-0.9
	7:3FTCA	$C_7F_{15}CH_2CH_2COOH$	NA	NA	NA	<1	<1-2
	5:2sFTOH	$C_5F_{11}CFCH(OH)CH_3$	NA	NA	NA	NA	<0.1-1.6
	7:2sFTOH	$C_7F_{15}CFCH(OH)CH_3$	NA	NA	NA	<0.4	<0.2-0.5
	6:2FTOH	$C_6F_{13}CH_2CH_2OH$	<1	<1-4	<1	<1	<0.3-0.6
	8:2FTOH	$C_8F_{17}CH_2CH_2OH$	<0.4-3.3	<0.4-5.0	<0.4-7.0	<0.4	<0.2-1.3
	10:2FTOH	$C_{10}F_{21}CH_2CH_2OH$	<0.6	<0.6-3.0	<0.6-10	<0.6	<0.3-8.1
	4:2FTS	$C_4F_9CH_2CH_2SO_3H$	NA	NA	NA	<0.3	<0.3
	6:2FTS	$C_6F_{13}CH_2CH_2SO_3H$	NA	NA	NA	<0.4-47	<0.4-57
	8:2FTS	$C_8F_{17}CH_2CH_2SO_3H$	NA	NA	NA	<0.7	<0.7

*NA: Not analyzed

For analysis of target chemicals except for *N,N*-Me2FOSA, 5:2sFTOH, 7:2sFTOH, 6:2FTOH, 8:2FTOH, and 10:2FTOH, 500 mL of water sample was alkalized by 0.2 g of sodium carbonate, and internal standards ($^{18}O_2$-PFHxS, $^{13}C_4$-PFOS, $^{13}C_4$-PFOSi, $^{13}C_8$-FOSA, d$_3$-*N*-MeFOSA, d$_5$-*N*-EtFOSA, d$_3$-*N*-MeFOSAA, d$_5$-*N*-EtFOSAA, d$_7$-*N*-MeFOSE, d$_9$-*N*-EtFOSE, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-8:2FTUCA, $^{13}C_2$-

8:2FTCA, and $^{13}C_2$-6:2FTS) were added into the sample. The sample was centrifuged at 3,000 rpm for 10 min, then the supernatant was transferred to a polypropylene reservoir equipped to a preconditioned Oasis HLB plus cartridge onto a Sep-Pak concentrator, and was passed through at a flow rate of 10 mL/min. The cartridge was centrifuged at 3,000 rpm for 10 min to remove water, then target chemicals were eluted with 3 mL methanol (MeOH) into a test tube. Target compounds remained in the centrifuge residue (particle phase) were extracted by ultrasonic vibration for 10 min with 10 mL MeOH. After centrifugation at 3,000 rpm for 10 min, the supernatant was transferred into a glass flask. This extraction process was repeated twice in the same manner. The inner wall surface of the sampling bottle and the reservoir were rinsed with 10 mL MeOH, and then combined with the ultrasonic extract into the glass flask. The solution was concentrated to 2 mL using a rotary vacuum evaporator at 36°C, and mixed to the eluate in the test tube. The combined extract was concentrated to 0.5 mL under a gentle stream of N_2 gas at 36°C, and 0.5 mL of methanol and 0.1 mL of 0.1% formic acid were added. The extract was passed through a cellulose-acetate membrane filter (0.20 μm pore size), and transferred into a glass vial. The target chemicals were measured by LC/MS[11] (Waters 2695 / Micromass ZMD2000) in 2009-2011 and LC/MS/MS[10] (Waters ACQUITY UPLC H-Class / Xevo TQD) in 2013-2017.

Results and discussion:
Concentration ranges and geometric mean (GM) concentrations of PFASs were shown in Table 1 and Figures 1-2, respectively. From 2009 to 2017, GM concentrations of PFOS were gradually decreased from 5.9 to 1.5 ng/L (Fig. 1). Both of GM concentrations of FOSA and *N*-MeFOSA, which are precursors of PFOS, were 0.8 ng/L in 2009. GM concentrations of most precursors were below the detection limits. The concentrations of PFOS and its precursors decreased in recent years. GM concentrations of PFBS and PFHxS, which have shorter fluoroalkyl chains than PFOS, ranged from 0.9 to 1.2 and 0.9 ng/L in 2015-2017, respectively. From 2009 to 2017, GM concentrations of PFOA were 6.7, 5.9, 7.7, 3.6, and 4.2 ng/L in 2009, 2011, 2013, 2015, and 2017, respectively (Fig. 2). These results suggested that the regulations on PFOS and PFOA caused the decreases in concentration of those chemicals in river water.

The highest concentration (1,300 ng/L) of PFOA was found at a sampling site in 2013 (Table 1), that was affected by effluent from a chemical factory. 8:2FTOH that is a precursor of PFOA, was detected in the GM concentration of 0.5 ng/L in 2013. On the one hand, other PFCAs (PFPeA, PFHxA, PFHpA, and PFNA) were also detected in 2015 and 2017, at the GM concentrations ranging from 1.0 to 2.6 and from 1.7 to 4.0 ng/L in 2015 and 2017, respectively. 6:2FTS used for metal plating, was detected in river water at the maximum concentration of 57 ng/L in 2017 (Table 1). It was known that 6:2FTS was biotransformed to 5:3FTCA and
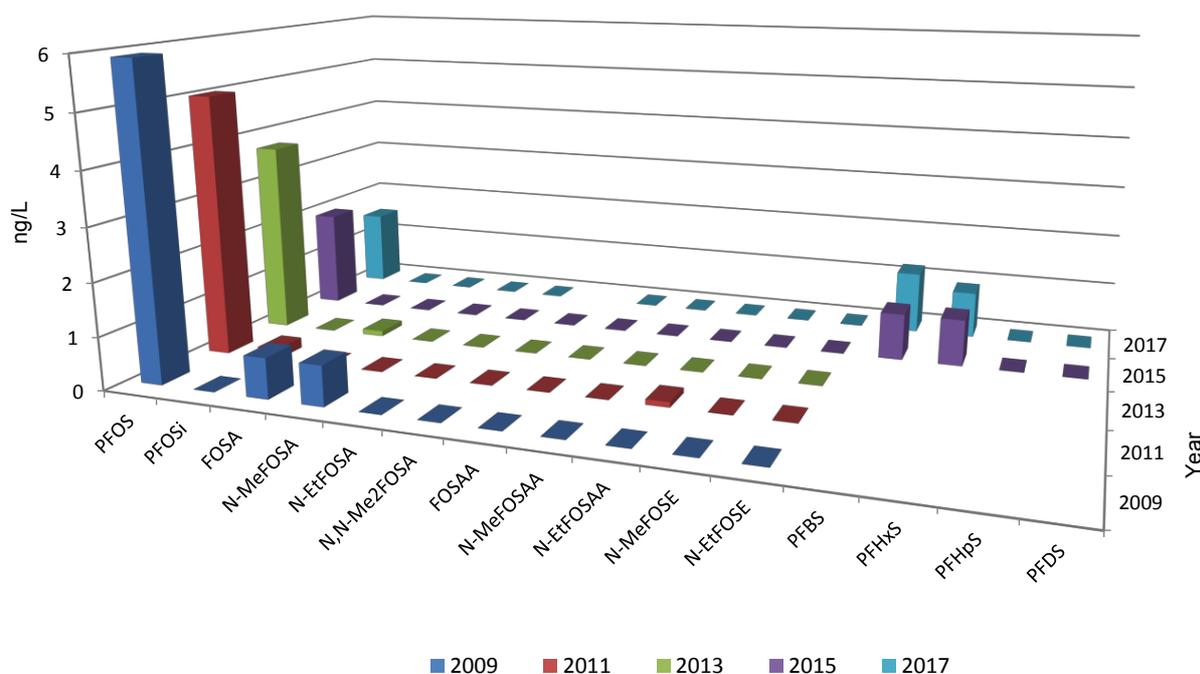
Figure 1: Geometric mean concentrations of PFSAs and the precursors
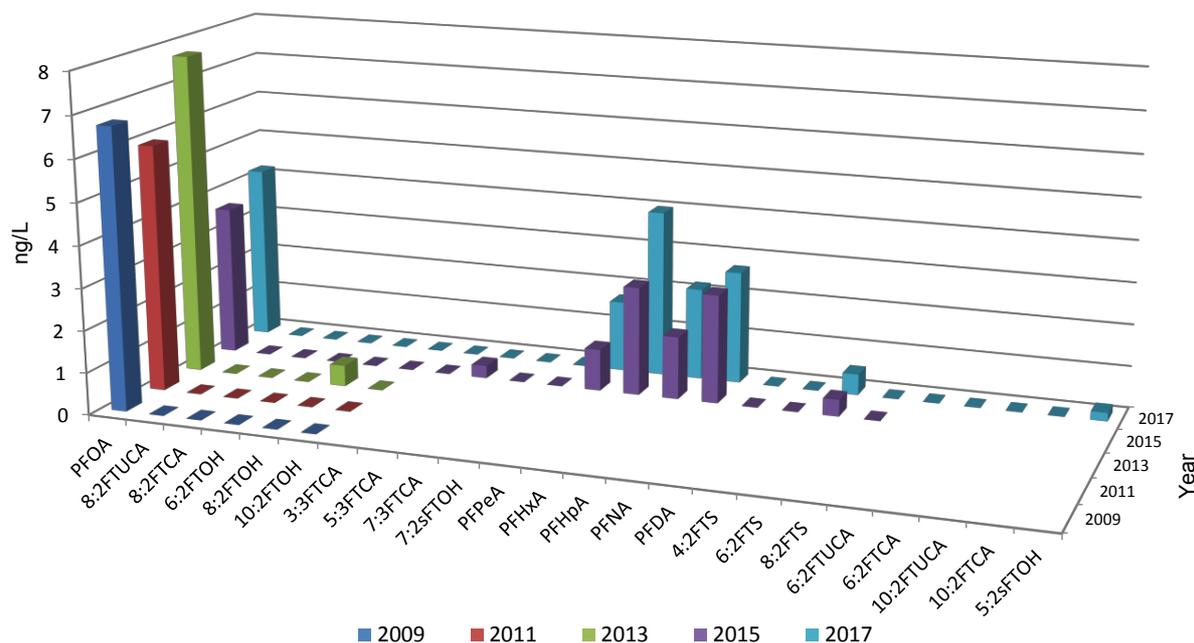
Figure 2: Geometric mean concentrations of PFCAs and the precursors

5:2sFTOH under aerobic condition in activated sludge of waste water treatment plants[12]. In this study, 5:3FTCA and 5:2sFTOH were also detected at GM concentrations of 0.3 and 0.2 ng/L in 2015 and 2017, respectively. The USEPA established the drinking water health advisory level at 70 ng/L for PFOS and PFOA in 2016[13]. In this study, the sum of PFOS and PFOA concentrations in river water slightly exceeded the level at a sampling site in 2017. Continuous monitoring of PFASs in river water is required in the future.

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