

OCCURRENCE OF PERFLUORINATED COMPOUNDS IN EFFLUENT FROM LARGE AND SMALL SCALE WASTEWATER TREATMENT PLANTS IN SAITAMA, JAPAN

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Introduction

Since 1950s, perfluorinated compounds have been widely used for commercial and industrial applications such as surfactants, lubricants, paper and textile coatings, and fire-fighting foams. Recently, many researchers reported a worldwide distribution of perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA) in surface water, groundwater, sediment, and biota^{1,2}. PFOS and PFOA are persistent accumulating in the environment, and thus affecting organisms³⁻⁵. C8-perfluorinated compounds such as 2-perfluorooctyl ethanol (8:2FTOH) and *N*-methylperfluoro-1-octanesulfonamide (*N*-MeFOSA) are precursors of PFOA and PFOS, respectively. These precursors are also used for commercial and industrial applications, and are thought to be breakdown to PFOA or PFOS in the environment^{6,7}. PFOS, PFOA and their precursors were detected from rain water, river water, and wastewater treatment plant (WWTP) effluent⁸. In Japan, several types of domestic WWTPs have developed scale in proportion to community population. A large-scale wastewater treatment plant (LWWTP) is suitable for municipal area with large population density, and a small-scale wastewater treatment plant (SWWTP) is suitable for small population area. Domestic wastewater are generally treated by these WWTPs, moreover a LWWTP is often received industrial effluents. Although many studies have focused on occurrences of PFOS and PFOA in WWTP effluents⁹⁻¹², little is known about the source of their precursors. Moreover, few researchers have determined concentrations of PFOS, PFOA and their precursors in effluent of SWWTP which received domestic wastewater from about 1,000 residents. This work presented that the occurrence of 'PFOS, PFOA and their 11 precursors (PFCs)' in effluents from SWWTP and LWWTP and estimation daily PFOS and PFOA emission per capita.

Materials and methods

Sampling

Seven LWWTPs and 10 SWWTPs in Saitama Prefecture located on the north of Metropolitan Tokyo, Japan were surveyed. The WWTP effluent samples were collected from April, 2009 to February, 2012. The details of WWTPs were shown in Table 1. Approximately 500 ml of grab effluent sample was poured into a screw cap polypropylene bottle. The samples were stored at 4°C until analysis.

Chemicals and reagents

Standard chemicals of PFOS, and PFOA were purchased from Kanto Chemical Co. (Japan) and Wako Pure Chemical Ind. (Japan), respectively. Nine

Table 1 Characteristics of WWTPs

| WWTP | Sampling date | Serving population | Flow volume (m ³ /day) | Per capita daily flow (m ³ /capita/day) |
|------------|---------------|--------------------|-----------------------------------|--|
| LWWTP-A | 20-Apr-09 | 320,754 | 128,763 | 0.40 |
| LWWTP-B | 21-Apr-09 | 15,251 | 3,411 | 0.22 |
| LWWTP-C | 21-Apr-09 | 33,084 | 9,688 | 0.29 |
| LWWTP-D | 17-Apr-09 | 1,227,047 | 390,922 | 0.32 |
| LWWTP-E | 20-Apr-09 | 110,793 | 41,155 | 0.37 |
| LWWTP-F | 7-Oct-10 | 1,279,666 | 459,868 | 0.36 |
| LWWTP-G | 14-Oct-10 | 47,870 | 16,920 | 0.35 |
| Geo. Mean* | - | 145,002 | 47,338 | 0.33 |
| SWWTP-A | 1-Oct-10 | 879 | 220 | 0.25 |
| SWWTP-B | 20-Dec-10 | 1,217 | 380 | 0.31 |
| SWWTP-C | 20-Dec-10 | 1,075 | 338 | 0.31 |
| SWWTP-D | 20-Dec-10 | 1,269 | 449 | 0.35 |
| SWWTP-E | 20-Dec-10 | 904 | 351 | 0.39 |
| SWWTP-F | 20-Dec-10 | 1,050 | 411 | 0.39 |
| SWWTP-G | 20-Feb-12 | 1,000 | 432 | 0.43 |
| SWWTP-H | 20-Feb-12 | 1,191 | 494 | 0.41 |
| SWWTP-I | 20-Feb-12 | 1,370 | 808 | 0.59 |
| SWWTP-J | 20-Feb-12 | 937 | 395 | 0.42 |
| Geo. Mean* | - | 1,078 | 407 | 0.38 |

*Geo. Mean: Geometric mean

PFOS precursors include perfluorooctane sulfinic acid (PFOSi), perfluoro-1-octanesulfonamide (PFOSA), *N*-MeFOSA, *N*-ethylperfluoro-1-octanesulfonamide (*N*-EtFOSA), perfluoro-1-octanesulfonamidoacetic acid (PFOSAA), *N*-methylperfluoro-1-octanesulfonamidoacetic acid (*N*-MeFOSAA), *N*-ethylperfluoro-1-octanesulfonamidoacetic acid (*N*-EtFOSAA), 2-(*N*-methylperfluoro-1-octanesulfonamido)-ethanol (*N*-MeFOSE), and 2-(*N*-methylperfluoro-1-octanesulfonamido)-ethanol (*N*-EtFOSE), and 2 PFOA precursors include 2H-perfluoro-2-decanoic acid (8:2FTUCA), and 2-perfluorooctyl ethanoic acid (8:2FTCA) were purchased from Wellington Laboratories, Inc. (Canada). $^{13}\text{C}_4$ -PFOS, $^{13}\text{C}_4$ -PFOSi, d_3 -*N*-MeFOSA, d_5 -*N*-EtFOSA, d_3 -*N*-MeFOSAA, d_5 -*N*-EtFOSAA, d_7 -*N*-MeFOSE, d_9 -*N*-EtFOSE, $^{13}\text{C}_4$ -PFOA, $^{13}\text{C}_2$ -8:2FTUCA, and $^{13}\text{C}_2$ -8:2FTCA used as internal standards were also purchased from Wellington Laboratories, Inc. Reagents used in this study were of residual pesticide analysis grade.

Sample treatment

Water sample (500 ml) was alkalized by 0.2 g of sodium carbonate, and 11 internal standards (each 4.5-50 ng) were added into the sample. The sample was filtrated through a glass fiber filter (1 μm pore size). The filtered residue with glass fiber filter was put into a 10 ml glass centrifuge tube, and extracted by ultrasonic vibration for 10 min with 5 ml of methanol. The extract was centrifuged at 3,000 rpm for 10 min, then the supernatant was transferred to a 100 ml flask. This extraction was repeated twice in the same manner. The filtrate was passed through a preconditioned Oasis HLB plus cartridge (Waters Co., USA) at a flow rate of 10 ml/min. To remove water, the cartridge was centrifuged at 3,000 rpm for 10 min, then target chemicals were eluted with 3 ml methanol into a 10 ml glass centrifuge tube. Glass wares used for the filtration and the screw cap polypropylene bottle used for sampling were rinsed with adequate amounts of methanol, and the rinsed solution was combined with the eluate into the 100 ml flask. The eluate was concentrated to 2 ml using a rotary vacuum evaporator at 40°C, and transferred to the 10 ml glass centrifuge tube. The combined extract was concentrated to 0.5 ml under a gentle stream of N_2 gas at 40°C, and 0.5 ml of methanol and 0.1 ml of 0.1% formic acid were added to the extract.

Instrumental analysis

A simultaneous analysis for PFCs was performed using a HPLC (Waters 2695, Waters Co.) / MS (ZMD2000, Micromass, UK) system, equipped with a ZORBAX Eclipse XDB C18 column (Agilent Technologies, Inc., USA), which was 150 mm in length, 2.1 mm in inner diameter, and 3.5 μm particle size. The column oven was kept at 40°C, and the flow rate of the mobile phase was 0.3 ml/min. The mobile phase consisted of solvent A (10 mM ammonium acetate) and solvent B (acetonitrile). The gradient was as follows: 30% B (0 min)–45% B in 5 min (held for 10 min)–85% B in 10 min (held for 3 min)–30% B in 2 min (held for 5 min). The total run time was 35 min. The injection volume was 20 μl . The measurement conditions of MS employed negative electrospray ionization (ESI-) with the selected ion monitoring mode, producing $[\text{M}-\text{H}]^-$ or $[\text{M}+\text{CH}_3\text{COO}]^-$ ions. The nitrogen gas flow rates for desolvation and cone were set at 600 l/h and 125 l/h, respectively. The temperatures of desolvation and ion source were 330°C and 135°C, respectively. The capillary voltage was fixed at 1.0 kV. The monitoring ion (the cone voltages) of each compound were as follows, PFOS: m/z 499 (-50 V), PFOSi: m/z 483 (-10 V), PFOSA: m/z 498 (-35 V), *N*-MeFOSA: m/z 512 (-35 V), *N*-EtFOSA: m/z 526 (-35 V), PFOSAA: m/z 556 (-40 V), *N*-MeFOSAA: m/z 570 (-30 V), *N*-EtFOSAA: m/z 584 (-30 V), *N*-MeFOSE: m/z 616 (-10 V), *N*-EtFOSE: m/z 630 (-10 V), PFOA: m/z 413 (-10 V), 8:2FTCA: m/z 477 (-10 V), 8:2FTUCA: m/z 457 (-10 V), $^{13}\text{C}_4$ -PFOS: m/z 403 (-50 V), $^{13}\text{C}_4$ -PFOSi: m/z 487 (-10 V), d_3 -*N*-MeFOSA: m/z 515 (-35 V), d_5 -*N*-EtFOSA: m/z 531 (-35 V), d_3 -*N*-MeFOSAA: m/z 573 (-20 V), d_5 -*N*-EtFOSAA: m/z 589 (-20 V), d_7 -*N*-MeFOSE: m/z 623 (-10 V), d_9 -*N*-EtFOSE: m/z 639 (-10 V), $^{13}\text{C}_4$ -PFOA: m/z

417 (-10 V), $^{13}\text{C}_2\text{-8:2FTUCA}$: m/z 479 (-10 V), and $^{13}\text{C}_2\text{-8:2FTCA}$: m/z 459 (-10 V). Concentrations of PFCs were quantified using the corresponding internal standard. For PFOSA and PFOSAA, $^{13}\text{C}_4\text{-PFOSi}$ was used as internal standard. The method detection limits (MDL) of those compounds ranged from 0.1 to 3 ng/l. The average of procedural recoveries and matrix recoveries of PFCs ranged from 85% to 119% and from 64% to 119%, respectively.

Results and discussion

Concentrations and detection frequency of PFCs in WWTP effluent

PFC concentrations and detection frequency in the effluent were shown in Table 2. PFOS and PFOA were detected in all effluents. Both of the geometric mean concentrations of PFOS and PFOA were higher in LWWTP effluent (11 ng/l for PFOS, and 23 ng/l for PFOA) than those in SWWTP effluent (2.1 ng/l for PFOS, and 9.1 ng/l for PFOA). The concentrations of PFOS and PFOA were same or lower order of magnitude as reported concentrations in WWTP effluents in Japan and other countries⁹⁻¹². Although PFOSi, PFOSA, *N*-MeFOSA, *N*-MeFOSAA, and *N*-EtFOSAA were detected in some LWWTP effluents, their concentrations and detection frequency were lower than those of PFOS and PFOA. On the other hand, PFOSi, PFOSA, *N*-MeFOSA, and 8:2FTUCA were detected in one or two SWWTP. It was thought that the high concentrations of PFCs detected in LWWTP caused by receiving industrial wastewater to LWWTP. *N*-EtFOSA, PFOSAA, *N*-MeFOSE, *N*-EtFOSE, and 8:2FTCA were not detected in all effluents. As PFOS was determined to be a persistent organic pollutant (POP) by the Stockholm Convention in May 2009, the production, import, export, and use of PFOS were strictly regulated. Nevertheless, PFOS is still detected in effluents from WWTP is a significant problem.

Table 2 Concentrations (ng/l) and detection frequency of PFCs in WWTP effluent

| Compounds | PFOS | PFOSi | PFOSA | <i>N</i> -MeFOSA | <i>N</i> -EtFOSA | PFOSAA | <i>N</i> -MeFOSAA | <i>N</i> -EtFOSAA | <i>N</i> -MeFOSE | <i>N</i> -EtFOSE | PFOA | 8:2FTUCA | 8:2FTCA |
|----------------|-------|-------|-------|------------------|------------------|--------|-------------------|-------------------|------------------|------------------|-------|----------|---------|
| MDL | 0.8 | 0.2 | 0.4 | 0.7 | 0.5 | 0.4 | 0.3 | 0.1 | 0.7 | 0.6 | 0.6 | 3 | 2 |
| LWWTP-A | 11 | <0.2 | 0.5 | <0.7 | <0.5 | <0.4 | 4.6 | <0.1 | <0.7 | <0.6 | 28 | <3 | <2 |
| LWWTP-B | 1.5 | 0.7 | 0.5 | <0.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 24 | <3 | <2 |
| LWWTP-C | 8.1 | <0.2 | 0.5 | <0.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 34 | <3 | <2 |
| LWWTP-D1 | 37 | <0.2 | 0.8 | 2.9 | <0.5 | <0.4 | 0.7 | <0.1 | <0.7 | <0.6 | 23 | <3 | <2 |
| LWWTP-D2 | 25 | 0.7 | 0.9 | 3.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 30 | <3 | <2 |
| LWWTP-E | 10 | <0.2 | 0.7 | 1.9 | <0.5 | <0.4 | 3.1 | <0.1 | <0.7 | <0.6 | 23 | <3 | <2 |
| LWWTP-F | 22 | 0.3 | <0.4 | <0.7 | <0.5 | <0.4 | <0.3 | 0.8 | <0.7 | <0.6 | 16 | <3 | <2 |
| LWWTP-G | 9.9 | <0.2 | <0.4 | <0.7 | <0.5 | <0.4 | <0.3 | 0.2 | <0.7 | <0.6 | 12 | <3 | <2 |
| Geo. Mean* | 11 | <0.2 | 0.5 | 0.8 | <0.5 | <0.4 | 0.4 | <0.1 | <0.7 | <0.6 | 23 | <3 | <2 |
| Detect. Freq** | 8/8 | 3/8 | 6/8 | 3/8 | 0/8 | 0/8 | 3/8 | 2/8 | 0/8 | 0/8 | 8/8 | 0/8 | 0/8 |
| SWWTP-A | 3.5 | <0.2 | <0.4 | <0.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 19 | <3 | <2 |
| SWWTP-B | 1.5 | <0.2 | <0.4 | <0.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 40 | <3 | <2 |
| SWWTP-C | 6.5 | <0.2 | <0.4 | <0.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 2.2 | <3 | <2 |
| SWWTP-D | 5.4 | <0.2 | 0.4 | <0.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 16 | 3 | <2 |
| SWWTP-E | 2.2 | <0.2 | <0.4 | <0.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 4.4 | <3 | <2 |
| SWWTP-F | 2.0 | <0.2 | <0.4 | <0.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 5.8 | <3 | <2 |
| SWWTP-G | 1.1 | 0.4 | <0.4 | 2.6 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 17 | <3 | <2 |
| SWWTP-H | 2.1 | <0.2 | 1.9 | 1.6 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 16 | <3 | <2 |
| SWWTP-I | 0.8 | <0.2 | <0.4 | <0.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 14 | <3 | <2 |
| SWWTP-J | 1.5 | <0.2 | <0.4 | <0.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 14 | <3 | <2 |
| Geo. Mean | 2.1 | <0.2 | <0.4 | <0.7 | <0.5 | <0.4 | <0.3 | <0.1 | <0.7 | <0.6 | 9.1 | <3 | <2 |
| Detect. Freq. | 10/10 | 1/10 | 2/10 | 2/10 | 0/10 | 0/10 | 0/10 | 0/10 | 0/10 | 0/10 | 10/10 | 1/10 | 0/10 |

*Geo. Mean: Geometric mean (Arbitrarily values below the MDL set to be half of the MDL)

**Detect. Freq: Detection frequency

Daily emission amounts of PFOS and PFOA per capita

Daily emission amounts of PFOS and PFOA per capita were estimated in 7 LWWTP and 10 SWWTP based on per capita daily flow ($\text{m}^3/\text{capita}/\text{day}$) and PFOS or PFOA concentration (ng/l) in the effluents (Table 3). PFOS daily

emission amounts widely ranged from 0.34 to 10.00 µg/capita/day for LWWTP, and from 0.46 to 2.05 µg/capita/day for SWWTP. For PFOA, these were 4.22 to 11.23 µg/capita/day for LWWTP, and 0.70 to 12.48 µg/capita/day for SWWTP. Both of the geometric means of PFOS and PFOA daily emission amount in LWWTP effluent (3.23 µg/capita/day for PFOS, and 7.25 µg/capita/day for PFOA) were higher than in SWWTP effluent (0.82 µg/capita/day for PFOS, and 4.30 µg/capita/day for PFOA). Although the contribution ratios of domestic and industrial wastewater in WWTP are not available, it seems that PFOS and PFOA amounts might partially consist of those from industrial wastewater in LWWTP. Takazawa *et al.* estimated daily PFOS and PFOA emission amounts for domestic human activities in the Tama River basin in Japan, and the estimation for PFOS and PFOA provided 1.6 and 2.9 µg/capita/day¹³). These values are similar to the values in this study.

Further study is needed to elucidate domestic origins of PFCs in wastewater treatment processes.

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Table 3 Estimated PFOS and PFOA daily emission amount

| WWTP | Unit: µg/capita/day | |
|------------|---------------------|---------------|
| | PFOS emission | PFOA emission |
| LWWTP-A | 4.29 | 11.23 |
| LWWTP-B | 0.34 | 5.33 |
| LWWTP-C | 2.37 | 9.87 |
| LWWTP-D | 10.00 | 8.40 |
| LWWTP-E | 3.85 | 8.56 |
| LWWTP-F | 8.03 | 5.90 |
| LWWTP-G | 3.51 | 4.22 |
| Geo. Mean* | 3.23 | 7.25 |
| SWWTP-A | 0.87 | 4.77 |
| SWWTP-B | 0.46 | 12.48 |
| SWWTP-C | 2.05 | 0.70 |
| SWWTP-D | 1.90 | 5.79 |
| SWWTP-E | 0.84 | 1.71 |
| SWWTP-F | 0.80 | 2.28 |
| SWWTP-G | 0.48 | 7.43 |
| SWWTP-H | 0.87 | 6.52 |
| SWWTP-I | 0.47 | 8.07 |
| SWWTP-J | 0.63 | 5.85 |
| Geo. Mean* | 0.82 | 4.30 |

*Geo. Mean: Geometric mean