BEHAVIORS OF 8:2 FLUOROTELOMER ALCOHOL AND THE BIOTRANSFORMATION COMPOUNDS IN SEWAGE TREATMENT PROCESSES

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Introduction

A fluorotelomer alcohol of *1H,1H,2H,2H*-perfluorodecanol (8:2FTOH), have been used as water/oil and stain repellents in consumer products including paints, coatings, textiles, and papers[1,2]. 8:2FTOH is biologically transformed into perfluorinated carboxylic acids (PFCAs) such as perfluorooctanoic acid (PFOA), and perfluoroheptanoic acid (PFHpA) via several intermediate metabolites of microbial metabolism in the aquatic ecosystems (Fig. 1)[3]. PFOA is a global persistent perfluorinated compound, accumulating in the environment, and thus affecting organisms[4,5]. Municipal and industrial wastewater treatment processes of sewage treatment plants (STPs) might have potentials of biotransformation from 8:2FTOH to PFCAs, thus STPs are thought to be a major point source of PFCAs[6]. Because PFCAs are stable during STP treatment, involving in the effluents, and releasing into the environment. Many mass balance studies have been conducted to elucidate the behaviors of PFCAs during the STP treatment process[6-10]. However, little is known about the fate of 8:2FTOH during STP treatment processes. 8:2FTOH and the biotransformation compound of 1-perfluoroheptyl ethanol (7:2 secondary) (7:2sFTOH) are semi-volatile, so generally detected in the atmosphere rather than the aquatic environment. Although these semi-volatile compounds should be distributed in aeration gas from the reaction tank of STPs, the mass contribution of gas phase is not known in STPs. This study presented that the fates and behaviors of 8:2FTOH and the 6 biotransformation compounds in the water and gas phases during wastewater treatment processes at 9 STPs.

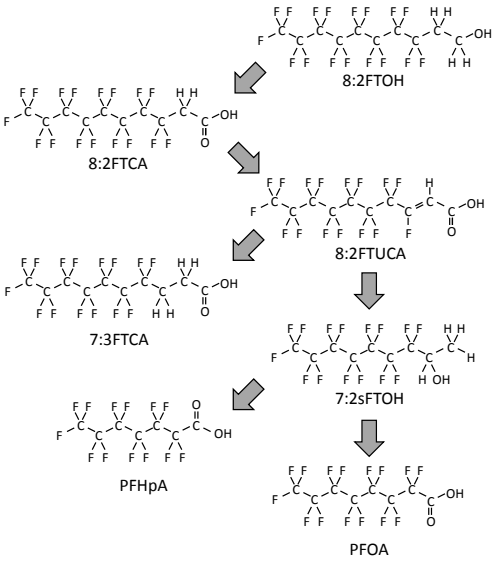


Fig. 1 Proposed aerobic biotransformation pathways of 8:2FTOH

Materials and methods

Sample collection

Nine STPs (STPs1-9) were surveyed in Saitama Prefecture, located on the north of Metropolitan Tokyo, Japan (Table 1). A conventional activated sludge (CAS) process was employed for small to large scale of sewage treatments in STP1-7 that serve a population of 44,200-1,730,000. An oxidation ditch (OD) process was employed for a small scale of sewage treatment in STP8-9 that serve a population of 15,300-33,900. Reaction tank gas volume of STP1-9 except STP5 ranged from 37,700-6,600,000 m^3/day. The reaction tank gas of STP1-7 was deodorized with activated carbons before discharging to the environment. However, no

Table 1 General information of STPs

ID	Sewage teatment	User population	Sewage volume (m^3/day)	Gas volume (m^3/day)
STP1	CAS[a]	1.73E+06	5.65E+05	6.60E+06
STP2	CAS	1.49E+06	4.82E+05	5.24E+06
STP3	CAS	1.25E+06	4.65E+05	3.62E+06
STP4	CAS	3.23E+05	1.44E+05	1.16E+06
STP5	CAS	1.11E+05	4.51E+04	No data
STP6	CAS	8.77E+04	5.66E+04	6.05E+05
STP7	CAS	4.42E+04	1.51E+04	1.05E+05
STP8	OD[b]	3.39E+04	1.12E+04	7.45E+04
STP9	OD	1.53E+04	4.82E+03	3.77E+04

[a] Conventional activated sludge process, [b] Oxidation ditch process

deodorizing facility was installed as the reaction tank gas treatment in STP8-9.

Influent water (IW), primary settling tank effluent water (PSW), reaction tank water (RW), secondary settling tank effluent water (SSW), and final effluent water (EW) samples were collected at each STP during July to October in 2013. Approximately 500 ml of grab sample was poured into a polypropylene (PP) centrifugal bottle for the analysis of 8:2FTCA, 8:2FTUCA, 7:3FTCA, PFOA, and PFHpA. For the analysis of 8:2FTOH and 7:2sFTOH, 60 l of reaction tank aeration gas (RG) was taken using a low-volume air sampler installed an SPE cartridge (InertSep RP-1) at the flow rate of 1 l/min. Moreover, deodorized gas (DG) was collected from STP4.

Sample treatment and analysis

For analysis of 8:2FTCA, 8:2FTUCA, 7:3FTCA, PFOA, and PFHpA, water sample (500 ml) was alkalized by 0.2 g of sodium carbonate, and 3 internal standards ($^{13}C_2$-8:2FTCA, $^{13}C_2$-8:2FTUCA, and $^{13}C_4$-PFOA; each 5-50 ng) were added into the sample. The sample was centrifuged at 3,000 rpm for 10 min, then the supernatant was transferred to a PP 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 compounds were eluted with 3 ml methanol (MeOH) into a test tube. Target compounds remained in the centrifuge residue 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 concentration of the 5 compounds was determined by use of a UPLC/MS/MS with slight modification of our previous report[11].

The extraction of 8:2FTOH and 7:2sFTOH in the water sample was, according to purge trap extraction method[11]. Briefly, 400 ml of water sample was gently poured into a 1000-ml gas washing bottle. An internal standard ($^{13}C_2$, d_2-8:2FTOH) 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 (XAD-2 and activated carbon) was aerated to the bottle, then extracted target compounds from water phase were trapped on an SPE cartridge (InertSep RP-1 mini). The target compounds were eluted with 3 ml of dichloromethane (DCM), and the eluate was concentrated to 0.5 ml under a gentle stream of N_2 gas at 30°C. 8:2FTOH and 7:2sFTOH in the SPE cartridge passed through aeration gas or deodorized gas were eluted with 3 ml of DCM into a glass test tube. The eluate was concentrated to 0.5 ml under a gentle stream of N_2 gas at 30°C, and transferred into a glass vial for GC/MS analysis. The details of measurement conditions of GC/MS were described in Motegi *et al.*[12]

Concentrations of 8:2FTOH, 8:2FTCA, 8:2FTUCA, and PFOA were quantified using the corresponding internal standard. 7:2sFTOH was quantified using $^{13}C_2$, d_2-8:2FTOH, and 7:3FTCA and PFHpA were quantified using $^{13}C_4$-PFOA. The method detection limits (MDL) of 7 compounds in water samples ranged from 0.3 to 2.6 ng/l, and 2 compounds in gas samples were 3 ng/m^3. The average recoveries were ranged from 89 to 123%.

Results and discussion

Concentrations of 8:2FTOH and the biotransformation compounds

Concentrations of 8:2FTOH and the biotransformation compounds in water and gas samples of sewage treatment processes in STPs were shown in Table 2. 8:2FTOH was detected in IW and PSW, ranging from 1.0 to 6.7 ng/l. No or low concentrations of 8:2FTOH were detected in SSW and EW, however, 8:2FTOH was detected in both RW and RG, suggesting most of 8:2FTOH might be biotransformed or volatilized in a reaction tank. The intermediate metabolites, 8:2FTCA and 8:2FTUCA were mainly detected in IW, PSW, and RW, in the range of <2.6-20 and <0.5-2.6 ng/l, respectively. In water phase, 7:2sFTOH was only detected in RW of 3 STPs in the range of 0.8-2.9 ng/l, but detected in RG of 9 STPs in the range of 61-191 ng/m^3, suggesting 8:2FTOH can be

Table 2 Average and ranges of concentrations of 8:2FTOH and the biotransformation compounds in water and gas samples in sewage treatment processes

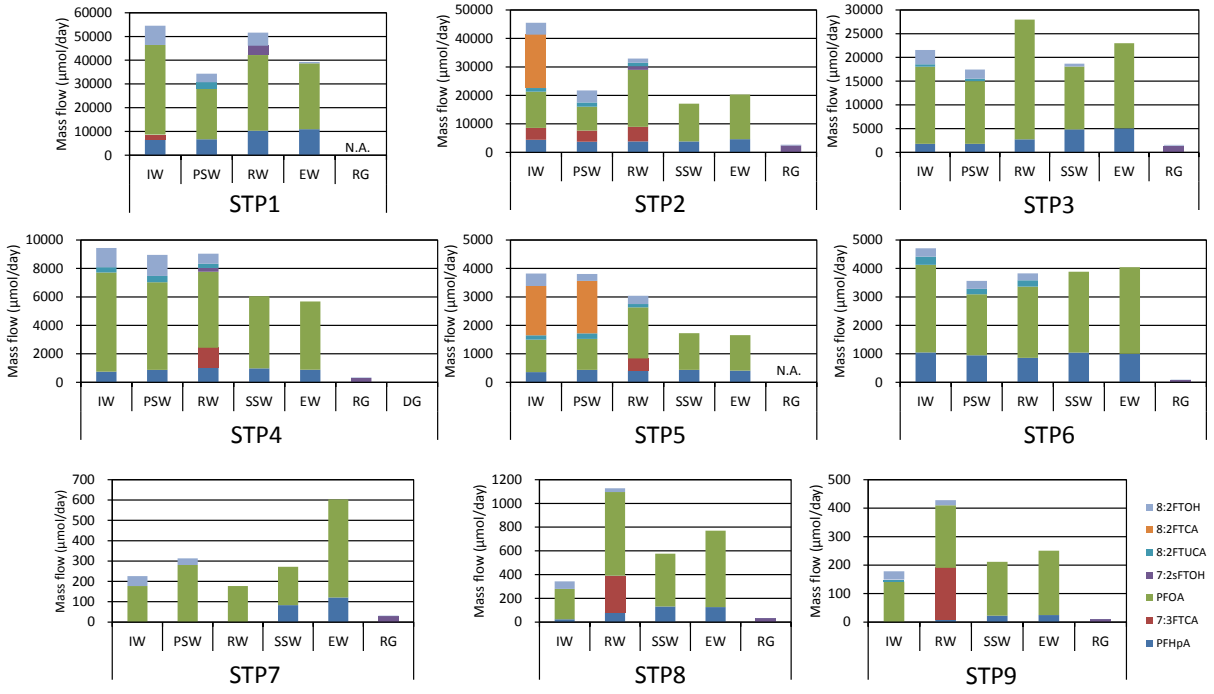
Sample type	STP (n)	Unit	PFHpA	7:3FTCA	PFOA	7:2sFTOH	8:2FTUCA	8:2FTCA	8:2FTOH
Influent water (IW)	9	ng/l	2.4 (1.0-6.7)	<1.0 (<1.0-3.8)	15 (4.9-28)	<0.4 (<0.4)	0.8 (<0.5-2.3)	4.1 (<2.6-19)	3.5 (1.5-6.7)
Primary settling tank efflulent water (PSW)	7	ng/l	2.4 (<0.3-4.3)	<1.0 (<1.0-3.6)	12 (7.2-18)	<0.4 (<0.4)	1.2 (<0.5-2.1)	3.3 (<2.6-20)	2.9 (1.0-4.7)
Reaction tank water (RW)	9	ng/l	2.9 (<0.3-6.6)	4.7 (<1.0-17)	18 (4.9-26)	0.5 (<0.4-2.9)	0.6 (<0.5-1.8)	<2.6 (<2.6)	1.8 (<0.4-4.5)
Secondary settleing tank effluent water (SSW)	8	ng/l	3.4 (1.7-6.7)	<1.0 (<1.0)	14 (5.2-21)	<0.4 (<0.4)	<0.5 (<0.5)	<2.6 (<2.6)	<0.4 (<0.4-0.6)
Final effluent water (EW)	9	ng/l	3.9 (1.9-7.0)	<1.0 (<1.0)	17 (11.5-24)	<0.4 (<0.4)	<0.5 (<0.5)	<2.6 (<2.6)	<0.4 (<0.4-0.5)
Raction tank gas (RG)	8	ng/m^3	N.A.	N.A.	N.A.	121 (61-191)	N.A.	N.A.	12 (3-23)
Deodorized gas (DG)	1	ng/m^3	N.A.	N.A.	N.A.	<3	N.A.	N.A.	<3

Values below the detection limits replaced with zero for calculating the average concentration.
Ranges in parentheses.

biotransformed to 7:2sFTOH via 8:2FTCA and 8:2FTUCA by microbial activity in the reaction tank. In STP4, the concentrations of 8:2FTOH and 7:2sFTOH in RG were 15 and 107 ng/m^3, respectively. The RG of STP4 was treated with activated carbons in a deodorization equipment. Both 8:2FTOH and 7:2sFTOH were not detected in the deodorized gas (DG), indicating that the activated carbon treatment of RG could be available to prevent the dispersion of fluorinated compounds from STPs to the environment. 7:3FTCA was mainly distributed in RW, but not detected in SSW and EW, suggesting 7:3FTCA was biotransformed to other metabolite or adsorbed to sludge in the reaction tank, because 7:3FTCA is less volatile. PFOA and PFHpA were detected in the most of water samples from 9 STPs in the ranges of 4.9-26 ng/l, and 0.6-7.0 ng/l, respectively.

Daily mass flows of 8:2FTOH and the biotransformation compounds

Molar basis daily mass flows of 8:2FTOH and the biotransformation compounds during the sewage treatment process of STPs were shown in Fig. 2. Total mass flows of target compounds in IW and EW widely varied from



IW: Influent water, PSW: Primary settling tank effluent water, RW: Reaction tank water, SSW: Secondary settling tank effluent water, EW: Final effluent water, RG: Reaction tank gas, DG: Deodorized gas, N.A.: Data not available

Fig. 2 Mass flows of 8:2FTOH and the biotransforming compounds during the sewage treatment processes in 9 STPs

187 (STP9) to 54,555 (STP1) µmol/day, and 250 (STP9) to39,275 (STP1) µmol/day, respectively. The mass flow ratios of EW to IW were ranging 45-107% in STP1-6, and 141-267% in STP7-9. It seems that a small scale STP or STP with OD treatment process increased mass flows of 8:2FTOH and the biotransformation compounds by sewage treatment processes.

PFOA was the dominant compounds in water samples among 8:2FTOH and the biotransformation compounds through the sewage treatment process. Most of EW was consisted of PFOA and PFHpA, and the rates were ranging 71-90% and 10-28%, respectively. A significant amount of 8:2FTCA was detected in IWs of STP2 and STP5, and disappeared in RW, suggesting at least biotransformation of 8:2FTCA progressed in a reaction tank. 7:3FTCA ratio in RW was higher in STP8-9 (27-43%) than those of the other STPs (0-16%). The transformation of 7:3FTCA from precursors might more progress in an OD process than in a CAS process.

The total mass flow ratio of 8:2FTOH and 7:2sFTOH in RG to the total discharge (the sum of the mass flow of 8:2FTOH and the biotransformation compounds in RW and RG) were 2-12%. Xiao *et al.*[13] modeled the fate of 8:2FTOH in STP based on fugacity analysis, suggesting 25% of 8:2FTOH can be emitted into the air in the aeration tank. It will be concerned an atmospheric dispersion of volatile or semi-volatile fluorinated compounds in the gas phase from STP without the activated carbon deodorization equipment.

Comparison of the biotransformation compounds ratios among different sewage treatment processes

The OD treatment process is one of an extended aeration activated sludge process in STP, and increased the ratios of end products such as PFOA, PFHxA from 8:2FTOH during the sewage treatment process. The 7:2sFTOH ratios in RG were higher in STP8-9 (98%) than that in other STPs (89-92%), suggesting more biotransformation from 8:2FTOH to 7:2sFTOH can occur in the OD process than those in the CAS process.

Further study is needed to elucidate the fates and behaviors of 8:2FTOH and the biotransformation compounds sewage treatment processes including the activated sludge in STP.

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