Detection, Occurrence, and Fate of Fluorotelomer Alcohols in Municipal Wastewater Treatment Plants

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Supporting Information

ABSTRACT: Fluorotelomer alcohols (FTOHs) are the most well-known precursors of perfluoroalkyl carboxylic acids (PFCAs), but limited information is available on their occurrence and fate in municipal wastewater treatment plants (WWTPs). The occurrence of FTOHs was investigated in influent, secondary effluent, and sludge of 12 municipal WWTPs in nine cities of China. FTOHs were detected in all WWTPs, and 8:2 FTOH was the predominant congener, with concentrations of 2.10–11.0 ng/L, 3.05–12.4 ng/L, and 0.36–1.91 ng/g dry weight in the influent, secondary effluent, and sludge, respectively. Relatively high proportions of long-chain FTOHs (C_{10-16}) were mainly detected in sludge samples. The mass balance of FTOHs and PFCAs in one of the WWTPs with an anaerobic-anoxic-oxic process was further explored. The decrease of mass loads was observed for 4:2 FTOH (mass change percentage: $21 \pm 3.3\%$), 8:2 FTOH ($22 \pm 1.5\%$), and 10:2 FTOH ($29 \pm 7.3\%$) through aerobic treatment, while the increase of mass loads was observed for 12 PFCAs from $18 \pm 16\%$ (perfluorononanoic acid) to $165 \pm 15\%$ (perfluorobutyric acid)), suggesting the potential biotransformation of FTOHs to PFCAs in the aerobic unit. This work provides the first report on the occurrence of FTOHs in sludge samples of municipal WWTPs and their mass balance and highlights a new emission route to environment via WWTPs.

INTRODUCTION

Fluorotelomer alcohols (FTOHs) are a class of important industrial intermediates used in the synthesis of fluorinated surfactants and polymeric materials and have been applied in a wide range of products such as paints, adhesives, waxes, polishes, metals, electronics, and caulks.¹ It has been reported the production volume of fluorotelomer increased substantially after the phase-out of PFOS and related products around 2000.² There is increasing evidence that FTOHs can cause endocrine disruptive effects in fish and human cells^{3–5} and reproduction impairment in fish and rat.^{3,6} In addition, FTOHs have been reported to be important precursors of perfluoroalkyl carboxylic acids (PFCAs), and transformation of FTOHs to PFCAs has been documented in different environments including activated sludge,⁷ rats,⁸ humans,^{9,10} and the atmosphere.¹¹ Previous studies have suggested that FTOHs might contribute to the increasing temporal trends of long-chain PFCAs ($C \geq 8$) in human serum¹⁰ and eggs of gulls.¹²

Previous studies have confirmed the global distribution of FTOHs in the air of Europe (181–288 pg/m³),^{9,13} North America (11–165 pg/m³),¹⁴ and Asia (51.4–1210 pg/m³).¹⁵ The first comprehensive investigation on FTOHs in water environment was conducted in 2008 in Osaka and Kyoto, Japan, and FTOHs were detected in rainwater (1.43–4.07 ng/

L), river water (<0.13–3.46 ng/L), and the effluents of wastewater treatment plants (WWTPs) (<0.13–6.67 ng/L).¹⁶ A recent study has investigated the mass flows and fates of per- and polyfluoroalkyl substances in the WWTP of a fluorochemical manufacturing facility,¹⁷ and the greatest mass flows were observed for 8:2 FTOH (1.5–166 g/d) and 10:2 FTOH (1.7–71 g/d). In spite of the detection of high concentrations (43.8–487 μg/L) of FTOHs in the influents of a European industrial WWTP, no target analytes were detected in the corresponding effluent.¹⁸ Given the fact that FTOHs are widely used for the production of consumer products, domestic wastewater discharge could be considered as one of their routes into the environment. However, the occurrence and fate of FTOHs in municipal WWTPs, particularly for sludge phase, has not yet been studied, partly due to the lack of sensitive analytical method.

In addition, significant increases in PFCA mass flows during activated sludge treatment has become a growing issue in WWTPs.^{19–23} Biodegradation of FTOHs to PFCAs during the

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treatment process has been proposed as a potential contributor to the increase of PFCAs in WWTPs.^{20–22} Microbial biodegradation from FTOHs to PFCAs has been well demonstrated in laboratory studies. For example, biotransformation of 8:2 FTOH to perfluorooctanoic acid (PFOA) has been observed in diluted activated sludge after 28-d incubation²⁴ and also in anaerobic digester sludge under methanogenic conditions.²⁵ Biotransformation of 6:2 FTOH to perfluorohexanoic acid (PFHxA) and perfluoropentanoic acid (PFPeA) has also been documented in diluted activated sludge²⁶ or anaerobic digester sludge.²⁵ While previous studies have highlighted the potential transformation of FTOHs to PFCAs on laboratory scale, the field evidence in municipal WWTPs is still not available.

In this study, the occurrence of six FTOHs (4:2, 6:2, 8:2, 10:2, 12:2, and 14:2 FTOH) in 12 municipal WWTPs of China and the behaviors of FTOHs and PFCAs over the course of the wastewater treatment process in a municipal WWTP in Wuxi City with an anaerobic-anoxic-oxic process (A/A/O; Plant A) were explored by mass balance analysis. Among them, due to the lack of standards of 12:2 FTOH and 14:2 FTOH, the two FTOH derivatives were semiquantified as shown in previous studies.^{27,28} In order to increase the analytical sensitivity, the ultra performance liquid chromatography-electrospray ionization-tandem mass spectrometry (UPLC-ESI-MS/MS) method based on dansylation^{28,29} was applied for the simultaneous determination of FTOHs in wastewater and sludge samples from municipal WWTPs. This study will improve our understanding on the fates and emission of FTOHs in municipal WWTPs.

MATERIALS AND METHODS

Chemicals and Reagents. The four target FTOHs 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH and four isotope-labeled standards (D_4 -4:2 FTOH, $^{13}C_2D_2$ -6:2 FTOH, $^{13}C_2D_2$ -8:2 FTOH, and $^{13}C_2D_2$ -10:2 FTOH) were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Formic acid (FA), dansyl chloride (DNS), and 4-(dimethylamino)pyridine (DMAP) were obtained from Sigma-Aldrich (St. Louis, MO, USA). HPLC-grade methanol (MeOH), acetonitrile (ACN), hexane, and dichloromethane (DCM) were purchased from Fisher Chemicals (New Jersey, USA). Oasis HLB (500 mg, 6 cc), Oasis WAX (60 mg, 3 cc) and Sep-Pak silica (1 g, 6 cc) solid-phase extraction (SPE) cartridges were purchased from Waters (Milford, MA, USA). Ultrapure water obtained by a Milli-Q RC Synthesis water purification system (Millipore, Bedford, MA, USA) was used in the experiments. Detailed information for chemicals and reagents for perfluoroalkyl acids (PFAAs) (including 12 PFCAs and five perfluoroalkyl sulfonic acids (PFSAs)) analysis is described in the [Supporting Information](#).

Sample Collection. Wastewater and sludge samples were collected from 12 municipal WWTPs (Plant A–Plant L) in nine cities of China from June 2014 to April 2016, with the detailed operational parameters of 12 municipal WWTPs and characteristics of wastewater and sludge in 12 municipal WWTPs shown in [Table S1](#) and [Table S2](#), respectively. Influent, secondary effluent, and return sludge samples were collected from Plant B–Plant L. Mass flow samples were collected from Plant A (anaerobic-anoxic-oxic, A/A/O) in Wuxi City, Jiangsu Province on 6, 7, and 8 June, 2014. Plant A serves about 820,000 inhabitants and treats about 100,000 m³ per day of mainly domestic wastewater. The treatment

processes in Plant A comprise screens, a horizontal-flow grit chamber, an upgraded A/A/O with suspended fillers in the latter half of the aerobic tank, and a secondary clarifier. The secondary effluent is further treated with rotary fiber disc filters (RDFDs), which is then designated as final effluent, before discharge to a receiving river. The characteristics of wastewater and sludge in Plant A are presented in [Table S3](#). Another 11 municipal WWTPs (Plant B–Plant L) were located in nine cities of China with the treatment capacity 60,000–2,000,000 m³/d and included three treatment processes (A/A/O, oxidation ditch (OD), and cyclic activated sludge technology (CAST)).

For all of the municipal WWTPs, no rain event had taken place in the previous week of the campaign or during sampling days. Flow-proportional (24 h) composite samples were collected using automatic samplers (SD900, HACH, Loveland, CO, USA), except for the sludge samples, which were collected three times per day and mixed together. The collected samples were stored in 1 L polypropylene (PP) containers with narrow mouths and screw tops that had been successively washed with ACN, ultrapure water Milli-Q (MQ) water, and then samples from the sampling points. The samples were kept in containers with dry ice and in the dark during the transport from sampling sites to the laboratory. Then the wastewater and sludge samples were centrifuged at the rotational speed of 9,000 rpm (J-25, Beckman Coulter, USA) for 10 min to separate wastewater from particulates. The supernatant was vacuum-filtered through glass microfiber filters (GF/F, Whatman, UK) according to previously published protocol,¹⁶ and then the wastewater samples were stored in the dark at 4 °C and extracted with SPE cartridges within 24 h to eliminate potential biodegradation of FTOHs. Sludge was then freeze-dried under vacuum (FD-1A-50, Boyikang, China) at low temperature (<−20 °C) to reduce potential biodegradation of FTOHs, homogenized with a mortar and pestle, sieved to obtain the desired particle size (diameter 0.5 mm), and stored at −20 °C, and the extraction was conducted in 1 week. All the samples were collected in triplicate, and extracts were analyzed with UPLC-MS-MS within one month.

Sample Preparation and Dansylation of FTOHs. FTOHs were determined based on a dansylation UPLC-MS-MS method as described in recent papers.^{28,29} However, the method has not been validated in wastewater or sludge samples, and therefore we optimized and applied the dansylation method to determine FTOHs in wastewater and sludge samples.

The water-compatible solvent extraction solvents (ACN, MeOH, 1:1 ACN/MeOH) were tested for extraction of FTOHs in sludge, and ACN showed the best extraction efficiencies ([Figure S1](#)). Thus, ACN was selected as the extraction solvent in the present study. For FTOH analysis in sludge, 0.5 g dw of freeze-dried samples spiked with 50 µL of D_4 -4:2 FTOH (10 µg/L), $^{13}C_2D_2$ -6:2 FTOH (10 µg/L), $^{13}C_2D_2$ -8:2 FTOH (10 µg/L), and $^{13}C_2D_2$ -10:2 FTOH (10 µg/L) was added to 15 mL PP centrifuge tubes. The samples were left to stand for 24 h at room temperature in the dark, and then 4 mL of ACN was added for extraction. After shaking for 20 min at 300 rpm and sonication for 20 min (40 °C), the extract was separated by centrifugation at 4000 rpm for 10 min. One milliliter of the extract was diluted with 4 mL of ultrapure water and then loaded on WAX cartridges which had been conditioned by 3 mL of ACN and 3 mL of ultrapure water. To reduce the elution volume for subsequent dansylation, we

used small WAX cartridges (60 mg, 3 cc), and 1 mL of ACN was sufficient to elute the target FTOHs from the cartridges (93–96% of different FTOHs were eluted). Then, 200 μL of DCM containing 30 mg/mL DNS and 30 mg/mL DMAP was added to the eluate, which was then shaken vigorously for 1 min. The resulting mixture was kept at 65 $^{\circ}\text{C}$ for 60 min, and then 3 mL of ultrapure water and 6 mL of hexane were added. After 10 min of shaking at 300 rpm, the organic layer was separated by centrifugation at 4000 rpm for 10 min. The extraction process was repeated twice, and the combined extracts were loaded onto silica cartridges conditioned with 8 mL of DCM and 8 mL of hexane. The dansylated FTOHs were eluted with 8 mL of hexane:DCM (v/v, 1:1), blown to dryness, and then dissolved in 0.2 mL of ACN for UPLC-MS/MS analysis.

FTOHs in wastewater samples (250 mL) were spiked with 50 μL of D_4 -4:2 FTOH (100 $\mu\text{g/L}$), $^{13}\text{C}_2\text{D}_2$ -6:2 FTOH (100 $\mu\text{g/L}$), $^{13}\text{C}_2\text{D}_2$ -8:2 FTOH (100 $\mu\text{g/L}$), and $^{13}\text{C}_2\text{D}_2$ -10:2 FTOH (100 $\mu\text{g/L}$). The water samples were passed through HLB cartridges which had been conditioned by 8 mL of ACN and 8 mL of ultrapure water at a flow rate of 1–2 drops/s. After the cartridges were dried under a flow of nitrogen, 5 mL of ACN was used to elute the analytes from the HLB cartridges. We used 0.5 mL of eluate for dansylation of FTOHs by adding 200 μL of DCM containing 30 mg/mL of DNS and 30 mg/mL of DMAP and 300 μL of ACN. The reaction solutions were cleaned up using the same strategy as the sludge samples, as mentioned above. Detailed sample preparation for PFAAs analysis is described in the [Supporting Information](#).

UPLC-ESI-MS/MS Analysis. The UPLC apparatus was an Acquity Ultra Performance Liquid Chromatography (Waters, Milford, MA, U.S.). Separation of dansylated FTOHs was conducted using a Waters ACQUITY UPLC BEH phenyl column (1.7 μm ; 2.1 mm $\times$ 100 mm). The column was maintained at 40 $^{\circ}\text{C}$, and the flow rate and injection volume were 0.3 mL/min and 10 μL , respectively. Methanol (A) and ultrapure water containing 0.1% formic acid (B) were used as mobile phases. The initial composition of 20% A was increased to 80% in 1 min, then increased to 100% at 5 min, maintained for 2 min, and followed by a decrease to 20% A, which was then held for 2 min to allow for equilibration. Mass spectrometry was performed using a Waters Micromass XEVO TQ MS (triple-quadrupole) detector operated with an electrospray ionization source (Micromass, Manchester, UK) in a positive ion mode. The optimized parameters were as follows: source temperature, 150 $^{\circ}\text{C}$; desolvation temperature, 350 $^{\circ}\text{C}$; capillary voltage, 3.00 kV; cone voltage, 30 V; desolvation gas flow, 800 L/h; cone gas flow, 50 L/h. Finally, data were acquired by multiple-reaction monitoring (MRM), and time-segmented scanning was used based on the chromatographic separation of target compounds to maximize detection sensitivity. The MRM transitions and mass spectrometry parameters of FTOHs derivatives and PFAAs in the triple quadrupole instrument are summarized in [Table S4](#). Detailed UPLC-ESI-MS/MS analysis for PFAAs is described in the [Supporting Information](#).

Quantification and Quality Assurance/Quality Control. Identification of the FTOHs was accomplished by comparing the retention time (within 2%) and the ratio (within 20%) of the two selected MRM ion transitions with those of standards. To automatically correct for analyte losses during extraction or sample preparation and to compensate for instrument response variations from injection to injection,

surrogate standards were used in this study. Concentrations of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH in wastewater and sludge samples were corrected using surrogate standards D_4 -4:2 FTOH, $^{13}\text{C}_2\text{D}_2$ -6:2 FTOH, $^{13}\text{C}_2\text{D}_2$ -8:2 FTOH, and $^{13}\text{C}_2\text{D}_2$ -10:2 FTOH, respectively. Due to the lack of standards of 12:2 FTOH and 14:2 FTOH, the two FTOH derivatives were semiquantified using the standard curve of the 10:2 FTOH derivative, as in previous studies,^{27,28} and $^{13}\text{C}_2\text{D}_2$ -10:2 FTOH was used as the surrogate standard. All equipment rinses were carried out with ACN to avoid sample contamination. One distilled water blank was incorporated in the analytical procedures for every batch of samples, but no background contamination was found. Recoveries of FTOHs in wastewater and sludge samples were calculated to assess the accuracy of the method, and the relative standard deviation (RSD) was used to evaluate precision. Since it is impossible to obtain sludge or wastewater samples free of analytes, recoveries ($n = 5$) were calculated by subtracting background concentrations in nonspiked samples from spiked samples. The spiked concentrations were 3–6 times higher than the background concentrations in samples, 50 ng/L for FTOHs in wastewater samples, and 20 ng/g dw for FTOHs in return sludge samples. Estimation of the limits of detection (LODs) were based on peak-to-peak noise of the baseline near the analyte peak obtained by analyzing field samples and on a minimal value of signal-to-noise of 3, while the limits of quantitation (LOQs) were signal-to-noise of 10. The extent of signal suppression and enhancement in UPLC-ESI-MS/MS was evaluated by spiking standards of dansylated FTOHs into the extracts of wastewater and sludge samples from SPE ($n = 5$), with an analyte addition at least three times the original concentration in samples. The matrix effect observed with each analyte was calculated using the percentage of signal intensity in the sample matrix versus the signal of the same concentration in pure solvent (ACN). Detailed Quantification and Quality Control for PFAAs analysis is described in the [Supporting Information](#).

Mass Balance Calculation. Mass balances were estimated by multiplying concentrations of each analyte by average daily flow rates according to the following equation

$$W = C_{\text{dissolved}} \times Q + C_{\text{adsorbed}} \times Q \times C_{\text{MLSS}}$$

where W is the total mass of one target analyte in the aqueous phase and adsorbed to sludge; $C_{\text{dissolved}}$ and C_{adsorbed} represent the dissolved and adsorbed concentrations, respectively; Q is water flow; and C_{MLSS} represents the concentration of mixed liquid suspended solids.

The mass change percentage (removal efficiency) for each analyte in each treatment unit was calculated as $(W_{\text{Inflow}} - W_{\text{Outflow}})/W_{\text{Inflow}} \times 100\%$, where W_{Inflow} and W_{Outflow} represent the mass load of an analyte in inflow and outflow, respectively.

The amounts of FTOHs released daily from the municipal WWTPs were calculated according to the following equation

$$\text{Mass} = (C_{\text{water}} \times Q_{\text{water}} + C_{\text{sludge}} \times Q_{\text{sludge}}) \times 10^{-6}$$

where Mass is the mass loading of an analyte (g/d); C_{water} (ng/L) and C_{sludge} (ng/g dw) are the concentrations of an analyte in the effluent and sludge, respectively; Q_{water} (m^3/d) is the daily flow of effluent; and Q_{sludge} (kg/d) is the daily flow of excess sludge.

DATA ANALYSIS

Concentrations less than LODs were reported as less than respective LOD (<LOD). For the calculation, the concentrations less than LODs were treated as zero, and values above the LODs but less than LOQs were assigned a value of half of the respective LOQ. Significance tests were conducted by *t* test. *P* values <0.05 were regarded as significant.

RESULTS AND DISCUSSION

Method Performance for Analyzing FTOHs and PFAAs in Wastewater and Sludge Samples. All FTOHs were detected, and the typical MRM chromatograms of FTOHs in sludge and secondary effluent after dansylation and cleanup are presented in Figure S2.

Recoveries of 4:2, 6:2, 8:2, and 10:2 FTOH were 84–112%, 83–116%, and 91–103% in influent, secondary effluent, and sludge samples, with RSDs less than 8.3% (Table S5). Besides the recoveries, method sensitivity and matrix effects are also important issues. Background contamination was not found, and the LODs for FTOHs in the influent, secondary effluent, and sludge were in the range of 0.05–0.12 ng/L, 0.03–0.11 ng/L, and 0.01–0.07 ng/g dw, respectively (Table S5). The LODs of FTOHs in wastewater and sludge were 100–1000-fold lower than LOQs in wastewater (50–100 ng/L) and sludge (50–100 ng/g dw) of recent methods by GC/MS,¹⁷ highlighting the application potential of the present method for determination of low concentrations of FTOHs in environmental samples.

The potential signal suppression and enhancement of FTOHs in UPLC-ESI-MS/MS detection was also evaluated. The matrix effect for all target analytes was minor, with −5.9 to 14% in influent, −3.2 to 9.9% in secondary effluent, and −8.4 to 9.1% in sludge (Table S5). The improvement in matrix effects was particularly important for the analysis of FTOHs, since signal suppression is a general problem for FTOH analysis using LC-ESI-MS/MS without dansylation, due to their low efficiency in ionization.³⁰

Recoveries of PFAAs were 73–109%, 72–106%, and 72–105% in influent, secondary effluent, and sludge samples (Table S6), with RSDs less than 12%. LODs for PFAAs in the influent, secondary effluent, and sludge were in the range of 0.06–0.23 ng/L, 0.03–0.18 ng/L, and 0.05–0.22 ng/g dw, respectively (Table S6).

Occurrence and Profiles of FTOHs in 12 Municipal WWTPs. Five among the six FTOHs (exception of 14:2 FTOH) were detected in the wastewater samples of the 12 municipal WWTPs, with total concentrations of four FTOHs (Σ FTOHs, 4:2 FTOH–10:2 FTOH) ranging from 3.78 to 15.1 ng/L in the influent and 3.70–17.9 ng/L in the secondary effluent. 8:2 FTOH was the predominant FTOH detected in all of the wastewater samples (2.10–12.4 ng/L) with a detection frequency of 100%, followed by 10:2 FTOH (<0.03–4.63 ng/L) with a detection frequency of 79% in the influent and 73% in the secondary effluent (Figure 1(a), Figure S3, and Table 1). The domination of 8:2 FTOH in wastewater was similar to that in air over a WWTP in Tianjin,³¹ but the profile of FTOHs was different from those in air samples over a WWTP in Ontario, in which 6:2 FTOH was the predominant FTOH.³² This should be partly due to the different emission profiles of FTOHs between Tianjin and Ontario. On the other hand, the high concentrations of 6:2 FTOH in air samples relative to the other FTOHs should be partly attributed to the higher vapor pressure of 6:2 FTOH (876 ± 159 Pa) than 8:2 FTOH (227 ± 35 Pa)

Figure 1. Concentrations and distributions of FTOHs in influent (a) and sludge (b) samples from 12 municipal WWTPs. Due to the lack of standards of 12:2 FTOH and 14:2 FTOH, the two FTOH derivatives were semiquantified.

and 10:2 FTOH (53 ± 7 Pa) and thus lead to preference partition of 6:2 FTOH from water to air.³³ One study has reported the occurrence of 8:2 FTOH and 10:2 FTOH in WWTP effluents in Japan, and the concentrations (<0.2–3.24 ng/L for 8:2 FTOH and <0.2–4.06 ng/L for 10:2 FTOH) were comparable to the present study.¹⁶ Another study investigated the occurrence of FTOHs in an effluent sample from a municipal WWTP and an influent sample as well as the corresponding effluent sample from an industrial WWTP. It was found that 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were only detected in industrial influent with high average concentrations at 487, 84.4, and 43.8 μ g/L, respectively,¹⁸ which were much higher than municipal wastewater samples investigated in the present study. A very recent study reported the concentrations of FTOHs in wastewater and sludge samples in an industrial wastewater treatment plant of a fluorochemical manufacturing facility,¹⁷ but the wastewater treatment plant investigated in their study was not a common situation, and the concentrations of FTOHs were very high and chemical profiles might be very different from common municipal WWTPs. The difference in Σ FTOHs concentrations between the influents and secondary effluents was not significant ($p = 0.45$). Except

Table 1. Concentrations of FTOHs in Influent, Secondary Effluent, and Sludge from 12 Municipal WWTPs in China

	influent (ng/L, <i>n</i> = 14)				secondary effluent (ng/L, <i>n</i> = 15)				sludge (ng/g, <i>n</i> = 14)			
	range	mean	median	freq (%)	range	mean	median	freq (%)	range	mean	median	freq (%)
4:2 FTOH	<0.12 ^a –0.40	0.29	0.34	79	0.15–0.35	0.29	0.32	80	0.01–0.20	0.07	0.05	100
6:2 FTOH	0.56–2.28	1.26	0.90	100	0.49–0.98	0.64	0.56	100	0.27–11.4	1.29	0.51	100
8:2 FTOH	2.10–11.0	5.72	5.09	100	3.05–12.4	5.27	3.79	100	0.36–1.91	1.18	1.16	100
10:2 FTOH	0.12–4.23	1.24	1.12	79	<0.03–4.63	1.07	0.57	73	0.32–2.40	0.92	0.50	100
ΣFTOHs ^b	3.78–15.1	8.51	7.45	NA ^c	3.70–17.9	7.28	5.77	NA	1.07–12.7	3.47	2.44	NA
12:2 FTOH	<0.06–0.80	0.15	<0.06	36	<0.05–0.34	0.02	<0.05	6.7	0.28–0.85	0.45	0.38	100
14:2 FTOH	<0.09	<0.09	<0.09	0	<0.08	<0.08	<0.08	0	<0.05–0.56	0.24	0.32	57

^a<*x*: concentrations less than respective LOD. ^bΣFTOHs: the total concentrations of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH. ^cNA: not available. Due to the lack of standards of 12:2 FTOH and 14:2 FTOH, the two FTOH derivatives were semiquantified.

Figure 2. Profiles of FTOHs in wastewater, sludge, and air. The FTOH concentrations in wastewater and sludge were from this study; the FTOH concentrations in air were from ref 31. Due to the lack of standards of 12:2 FTOH and 14:2 FTOH, the two FTOH derivatives were semiquantified.

for 6:2 FTOH, which showed significantly lower concentrations in the secondary effluent ($p = 0.01$), the other FTOHs did not exhibit significant differences between the influents and secondary effluents (p values: 0.12–0.95). These results indicated that FTOHs could not be efficiently removed by municipal WWTPs.

All FTOHs were detected in the sludge samples from 12 municipal WWTPs, with a detection frequency of 100% except for 14:2 FTOH (57%). To our knowledge, only one study reported the occurrence of FTOHs in wastewater samples from the WWTP,¹⁶ and so this is the first report on the occurrence of FTOHs in sludge of municipal WWTPs, and the concentrations of ΣFTOHs in sludge were 1.07–12.7 ng/g dw. It was similar to wastewater samples; 8:2 FTOH was detected as the predominant congener in sludge samples, with an average concentration of 1.18 ng/g dw (Figure 1(b) and Table 1). It should be noted that the concentrations of FTOHs in sludge samples were lower than the LODs (50–100 ng/g dw) of recent methods by GC/MS,¹⁷ showing that the sensitive derivatization method developed in the present study was critical for the determination of FTOHs in environmental matrices with low concentrations. In contrast to the wastewater samples, long-chain FTOHs including 10:2 FTOH (0.32–2.40 ng/g dw), 12:2 FTOH (0.28–0.85 ng/g dw), and 14:2 FTOH (<0.05–0.56 ng/g dw) were detected at relatively high

concentrations in the sludge samples (Figure 2). This phenomenon should be partly attributed to the preferential sorption of long-chain FTOHs to sludge from water, as indicated in previous laboratory studies,³⁴ that the increase of each CF₂ moiety decreased the aqueous solubility by ~0.78 log units. At the same time, in contrast to the occurrence of FTOHs (0.05–0.15 ng/g dw for 8:2 FTOH, 0.08–0.26 ng/g dw for 10:2 FTOH) in six sediment samples from Liaodong Bay,²⁹ 8:2 FTOH (0.36–1.91 ng/g dw) and 10:2 FTOH (0.32–2.40 ng/g dw) in the present study were detected at relatively high concentrations. The observed preferential partition of the long-chain FTOHs in excess sludge highlighted an environmental risk for the application of dehydrated sludge on agriculture fields, as exemplified by the occurrence of FTOHs (5–73 ng/g dw for 8:2 FTOH, <5.6–166 ng/g dw for 10:2 FTOH, 2–133 ng/g dw for 12:2 FTOH, and 3–52 ng/g dw for 14:2 FTOH) in sludge-applied soils from the United States.²⁷ While the sludge analyzed was heavily polluted by a manufacturer,²⁷ combined with the wide occurrence of FTOHs in sludge samples determined in the present study, it was suggested that the potential environmental risk from the municipal WWTPs. Future studies are warranted to more broadly investigate the potential occurrence and risk of FTOHs in sludge-applied soils.

Figure 3. Total mass flow (g/d) of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH along the treatment processes in Plant A (A/A/O).

Figure 4. Mass change percentages (removal efficiency) of PFCAs and FTOHs in three treatment processes including anaerobic tank (a), anoxic tank (b), and aerobic tank (c) of Plant A (A/A/O). “*” indicates a statistically significant result.

Behaviors of FTOHs and PFCAs along Wastewater Treatment Process. The concentrations of FTOHs and PFAAs (including 12 PFCAs and 5 PFSAs) over the whole treatment process of Plant A(A/A/O) are presented in Table S7 and Table S8. Generally decreasing concentrations of

FTOHs in wastewater samples were observed along the treatment process. For example, the concentration of 8:2 FTOH was 10.4 ± 0.53 ng/L in the influent, 3.73 ± 0.15 ng/L in the anaerobic wastewater samples, and 2.99 ± 0.01 ng/L in the final effluent, indicating part of FTOHs from wastewater

may be transformed during the treatment. The concentrations of PFCAs were similar between influent and effluent, except for perfluorobutyric acid (PFBA) whose concentrations were increased from 24.8 ± 3.69 ng/L to 101 ± 13.1 ng/L. To better understand the behaviors of FTOHs in municipal WWTPs, we calculated the mass flow (wastewater and sludge) of FTOHs and PFCAs in Plant A (A/A/O) as shown in Figure 3 and Figure S4, as well as the mass change percentages of FTOHs and PFCAs in the three basic treatment units of Plant A, namely the anaerobic, anoxic, and aerobic tanks (Figure 4).

In the anaerobic tank, 4:2 FTOH, 6:2 FTOH, and 8:2 FTOH were found to be increased by $39 \pm 17\%$, $14 \pm 0.43\%$, and $25 \pm 0.47\%$, respectively, while 10:2 FTOH decreased significantly by $65 \pm 5.5\%$. In the anoxic tank, the mass loads of Σ FTOHs increased from 9.48 ± 0.07 g/d to 13.4 ± 0.26 g/d, with 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH increased by $36 \pm 24\%$, $1.8 \pm 13\%$, $73 \pm 1.9\%$, and $25 \pm 4.5\%$, respectively ($p < 0.05$ for 8:2 FTOH and 10:2 FTOH) (Figure 4(b)), suggesting the presence of some precursors of FTOHs such as polyfluoroalkyl phosphates (PAPs),³⁵ fluorotelomer acrylate (FTAC), and fluorotelomer methacrylate (FTMAC).³⁶ A previous study confirmed the presence of PAPs in sludge at high concentrations ranging from 47 to 200 ng/g.³⁷ Therefore, further study is warranted to clarify the potential occurrence of these upstream precursors in municipal WWTPs and their contribution to FTOH mass loads. In the aerobic tank, the mass loads of Σ FTOHs decreased from 13.4 ± 0.26 g/d to 10.5 ± 0.32 g/d, with 4:2, 8:2, and 10:2 FTOH decreased by $21 \pm 3.3\%$ ($p = 0.01$), $22 \pm 1.5\%$ ($p = 0.01$), and $29 \pm 7.3\%$ ($p = 0.03$), respectively (Figure 4(c)). This result showed that biodegradation of FTOHs might occur in aerobic tanks, which agreed with previous laboratory biodegradation tests.^{24,38,39} While it cannot be strictly excluded that such loss of FTOHs in the aerobic tank was due to emit into air as reported in previous studies,^{32,40–42} the significant loss of nonvolatile 10:2 FTOH at a similar extent to 4:2 FTOH, and also the specific loss of FTOHs in the aerobic tank, indicated that such mass decrease of FTOHs should be largely attributed to biodegradation.

As for PFCAs, while congener-specific increase or decrease in mass flows were found in the different units, the most pronouncing change was found in the aerobic tank where the mass flows of all 12 PFCAs increased. The mass loads of total PFCAs increased from 94.7 ± 4.43 g/d to 161 ± 4.23 g/d before and after the aerobic tank. The mass change percentages of all PFCAs in aerobic tank were in a range from $18 \pm 16\%$ (PFNA) to $165 \pm 15\%$ (PFBA) ($p < 0.05$ for PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFUnDA, and PFTrIDA) (Figure 4(c)). Such results were consistent with the significant loss of FTOHs in the same aerobic tank, indicating the potential biotransformation of FTOHs to PFCAs. Such preference biodegradation of FTOHs to PFCAs under aerobic conditions has been documented in previous laboratory studies.^{24,38,39} It should be noted that the increase of mass loads of PFPeA in aerobic tank was 6.29 ± 1.30 g/d, about 100-fold greater those (0.04 ± 0.00 g/d) of corresponding decreasing mass loads of precursor 4:2 FTOH. Such phenomenon showed that the mass increase of PFCAs could not be completely explained by the biotransformation of FTOHs, and future studies are warranted to clarify the potential biotransformation of other precursors such as PAPs.^{35,43,44} While previous studies have widely highlighted the potential biotransformation of FTOHs to PFCAs in laboratory experiments,^{24,39,45} with the molar yield of PFOA from 8:2 FTOH ranging from 0.5% in a pure bacterial

culture³⁸ to 40% in one aerobic soil,⁴⁶ the present study provided the field evidence for potential biotransformation of FTOHs to PFCAs in the aerobic treatment.

Discharge of FTOHs to Environment. Due to the lack of sludge discharge information on four plants (Plants B, D, E, F) in the 12 investigated municipal WWTPs, daily mass loadings of FTOHs (g/d) to environment from eight investigated municipal WWTPs are presented in Table S9. The discharge of Σ FTOHs (4:2 FTOH–10:2 FTOH) from the secondary effluent and sludge was calculated to be 0.30–35.8 g/d and 0.02–1.01 g/d, respectively. While aqueous discharge via effluent was the main discharge route for 4:2 FTOH (81–99%), 6:2 FTOH (77–96%), and 8:2 FTOH (81–99%), sludge discharge via excess sludge was the main discharge route for 12:2 FTOH (100%) and 14:2 FTOH (100%). The discharge of Σ FTOHs in effluent and sludge was calculated as 0.05–0.18 g per $10^4 \times \text{m}^3$ wastewater.⁴¹ The discharge of excess sludge without further treatment significantly contributes to the environmental burden of FTOHs, and further studies are warranted to effectively eliminate FTOH residuals in sludge.

Overall, this work provides the first report on the occurrence of FTOHs in sludge samples of municipal WWTPs and their mass balance and indicates part of the FTOHs may have been transformed to PFCAs in the aerobic tank. The emission data for FTOHs presented here is useful for justification of future waste sector studies. The decrease of the mass load of total FTOHs and the simultaneous increase of PFCAs in the aerobic tanks suggested the potential biotransformation of FTOHs to PFCAs, while FTOHs increase in the anoxic tank suggested that precursors of FTOHs may exist in wastewater, which will require further clarification.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b00315.

Text, figures, and tables of (1) chemicals and reagents, (2) sample preparation, (3) UPLC-ESI-MS/MS, and (4) quantification and quality control for PFAAs analysis; (5) comparison of FTOH concentrations in one same municipal sludge sample; (6) UPLC-MS/MS MRM chromatograms of FTOHs in standards after dansylation; (7) concentrations and distributions of FTOHs in secondary effluent samples from 12 municipal WWTPs; (8) total mass flow of 12 PFCAs along the treatment processes in Plant A (A/A/O); (9) operational parameters of 12 municipal WWTPs; (10) characteristics of wastewater and sludge in 12 municipal WWTPs; (11) characteristics of wastewater and sludge in Plant A (A/A/O); (12) MRM transitions and mass spectrometry parameters of FTOH derivatives and PFAAs in the triple quadrupole instrument; (13) LODs, LOQs, recoveries, and ME of FTOHs in wastewater and sludge; (14) LODs, LOQs, and recoveries of PFAAs in wastewater and sludge; (15) concentrations of FTOHs in wastewater and sludge samples of Plant A (A/A/O); (16) concentrations of PFAAs in wastewater and sludge samples of Plant A (A/A/O); (17) discharge of FTOHs from effluent and sludge of municipal WWTPs to environment (PDF)

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