Ubiquitous Occurrence of Fluorotelomer Alcohols in Eco-Friendly Paper-Made Food-Contact Materials and Their Implication for Human Exposure

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Supporting Information

ABSTRACT: The occurrence of fluorotelomer alcohols (FTOHs) was investigated in 94 food-contact materials (FCMs). We detected 6:2 FTOH (<0.60–1110 ng/g), 8:2 FTOH (<0.40–8490 ng/g), and 10:2 FTOH (<0.02–9350 ng/g) in most FCM samples, and four longer-chain C_{14–20} FTOHs were, for the first time, identified in FCMs with relatively high concentrations (<0.02–8450 ng/g for 12:2 FTOH, <0.02–1640 ng/g for 14:2 FTOH, <0.02–372 ng/g for 16:2 FTOH, and <0.02–130 ng/g for 18:2 FTOH). There were three typical profiles of FTOHs that were dominated by 6:2 FTOH (95.6 ± 8.1% in 9 FCMs), 8:2 FTOH (50.9 ± 20.8% in 22 FCMs), and 10:2 FTOH (44.5 ± 20.9% in 30 FCMs), indicating the congener-specific usage of FTOHs for different commercial purposes. All nine detectable FCMs produced in the United States were dominated by 6:2 FTOH, which was significantly different from those produced in China. The median concentration of total FTOHs in eco-friendly paper tableware was 2990 ng/g, which was lower than in popcorn bags (18 200 ng/g) but much higher than other FCMs (<0.55–38.7 ng/g). FTOHs could migrate from paper bowls, with migration efficiencies of 0.004–0.24% into water, 0.004–0.24% into 10% ethanol, 0.009–2.79% into 30% ethanol, 0.06–13.0% into 50% ethanol (v/v) simulants, and 0.04–2.28% into oil. Migration efficiencies decreased with increasing carbon chain lengths of FTOHs.

INTRODUCTION

Environmental pollution from polyfluorinated and perfluorinated compounds (PFASs) has received widespread attention due to their persistence and ubiquity in the environment and known toxicities such as developmental toxicity, decrease in birth weight, carcinogenicity, and liver damage.1–3 PFASs are widely used in commercial products, such as metal plating, firefighting foams, inks, clothing, textiles, and food-packaging materials.4 In Europe, 33% of PFASs are produced for packaging composed of paper or cardboard, and paper accounts for approximately 20% of all food packaging (coated paper: 17%, uncoated paper: 3.5%).5 Considering that PFASs in coated packaging might migrate into contacted foodstuffs, their residuals in food-contact materials (FCMs) have attracted attention.

Although residuals of PFAS additives in FCMs are of concern for human health, only perfluorinated carboxylic acids (PFCAs) have been detected in paper-made FCMs, especially in fast-food packaging and microwave popcorn bags.6 Fluorotelomer alcohols (FTOHs) are an important class of PFASs that are incorporated into the production of a majority of commercial fluorochemicals.7 Since the electrochemical fluorination (ECF) production method for fluorochemicals was gradually discontinued in the United States in 2003, the telomerization method has become the main industrial synthetic route, and as a result, FTOH-based additives are increasingly important in consumption products.8 FTOHs have been suggested to be important precursors of PFCAs because FTOHs can be metabolized to PFCAs in rats9 and humans10 or photodegraded in the atmosphere.11 Previous studies have suggested that fluorotelomer-based precursors might contribute to increasing temporal trends of longer-chain PFCAs in human populations.12 In addition, there is increasing evidence that FTOHs can impair fish reproductive functions by disrupting sex hormone synthesis13,14 and induce neural-tube defects in fetal and neonatal rats via utero exposure.15 However, the recognized occurrence of FTOHs in matrices of common exposure routes to humans was limited to air. Because FTOHs are used as starting materials for the synthesis of fluoronomers and polymers for food-contact coatings,16 humans would likely be exposed to FTOHs via releases from surfaces of FCM products, as exemplified by the high migration of FTOHs from microwave popcorn bags.17,18 In addition to microwave popcorn bags, there are many other paper-made FCMs such as paper tableware (including paper plates, paper bowls, and paper lunch boxes) and paper cups, which are used daily. Thus, there is a need to investigate the occurrence of FTOHs in FCMs and the potential contributions to human exposure.

In this study, residuals of FTOHs were examined in 69 daily-use paper-made FCMs produced in China, including paper tableware, paper cups, and paper boxes, paper bags,
microwave popcorn bags, and other FCMs, as well as an additional 25 FCMs (paper tableware, microwave popcorn bags, and paper cups) produced in the United States. To elucidate the extent of human exposure to FTOHs from FCMs, we further conducted migration tests of FTOHs from FCMs (paper tableware) to food simulants. For comparison, residuals and migration of PFCAs were also conducted. Results obtained in this study will be useful in understanding the exposure of FTOHs and PFCAs to humans.

**MATERIALS AND METHODS**

**Chemicals and Reagents.** A total of 13 perfluorocarboxylic acids (C4–C18), three fluorotelomer alcohols (6:2 FTOH, 8:2 FTOH, and 10:2 FTOH) and ten stable-isotope-labeled standards were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Detailed isotope-labeled standards were purchased from Wellington Laboratories in Beijing, China and online from 2013 of 69 paper-made FCMs were purchased from various commercial retailers in Beijing, China and online from 2013 to 2015 (Table S1).

**Sample Preparation of Food-Contact Materials.** A total of 69 paper-made FCMs were purchased from various commercial retailers in Beijing, China and online from 2013 to 2015 (Table S1). A total of 25 FCMs were purchased from various retail stores in Columbus, Ohio in 2015 (Table S1). Considering the potential sampling bias, all FCMs that were sold nationwide with the highest sales in both China and the United States were purchased from nationwide vendors or via the Internet for this study. Paper tableware made of plant fiber (such as sugar-cane and reed-pulp fiber) was labeled by “degradable”, “compostable”, and “eco-friendly”, and classified as eco-friendly samples in this study. PFAs were used for water- and oil-proofing agents in the printing inks. To exclude the influence of printing inks in multilayer composite paper samples and ivory board samples (white cardboard samples, e.g., hamburger boxes), we peeled off the printed outer surfaces from the samples before extraction; for other single-layer samples, the printed portions were cut from the samples before extraction (Table S1).

**Migration Tests for Paper Tableware.** Because paper-made FCMs are often used for fast food in snack bars and take-out food in restaurants, the contact with food is generally for short durations, and migration tests for a short time were conducted. Food simulants, including water, ethanol–water solutions (v/v: 10:90, 30:70, 50:50),44 and oil, were preheated to 100 °C in sealed screw-capped glass tubes. A total of 10 mL of food simulants was transferred to paper bowls and kept for 15 min at room temperature. Only the bottom of each paper bowl had contact with the food simulants (contact area was 36.32 cm²). Food simulants were removed from the paper bowls with glass pipettes for further treatment. The ethanol/water solutions (v/v: 70:30, 50:50) were diluted with 20 and 40 mL of ultrapure water before further treatment. A total of 1 mL of oil was extracted by 2 mL of methanol, and methanol extract was diluted with 6 mL of ultrapure water prior to further treatment. All food simulants were concentrated on WAX cartridges and treated by the same procedures as described above for FTOHs and PFCAs in FCMs. The migration test for each simulated sample was conducted in triplicate. The migration efficiencies to food simulants were calculated by the following equation.

migration efficiency(%) = \( \frac{\text{mass}_{\text{test}}}{(C_{\text{FCM}} \times S_{\text{test}}) \times 100} \)

where \( \text{mass}_{\text{test}} \) is the migration amount into 10 mL food simulants (ng), \( C_{\text{FCM}} \) is the original concentration of the paper bowl (ng/cm²), and \( S_{\text{test}} \) is the contact area in migration tests (cm²).

**Instrument Analysis.** All target chemicals were analyzed by a Premier XE tandem quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source, coupled to an Acquity Ultra Performance LC (Waters, Milford, MA). An ACQUITY UPLC system (Waters) coupled to a Xevo G2 QT system operated with ESI was used for the identification of daisy-lineated FTOHs. Detailed instrument conditions for analysis of daisy-lineated FTOHs, nonderivatized FTOHs, and PFCAs are described in the Supporting Information.

**Quantitation and Quality Control.** Identification of derivatized FTOHs (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) and PFCAs (C4–C18) using a triple-quadrupole instrument was accomplished by comparing the retention time (within 2%) and the ratio (within 20%) of the two selected multiple-reaction monitoring (MRM) ion transitions with those of standards. Identification of derivatized 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH using Q-TOF MS was accomplished by comparing the retention time (within 2%) and accurate...
mass (within ±5 ppm mass errors) with those of standards. The entire analytical procedures of derivatized FTOHs and PFCAs were checked for precision, reproducibility, linearity, blank contamination, matrix effects, and method-quantification limits (MQLs). A single procedural blank was analyzed per 10 FCM samples to assess potential sample contamination during the entire procedure. For food simulants (water and ethanol mixtures), procedural blanks (n = 3 for each) were prepared by substitution of 10 mL of ethanol/Milli-Q water (v/v, 0:10, 1:9, 3:7 and 5:5). For oil, procedural blanks (n = 3 for each) were prepared by substitution of 1 mL of oil. For FTOH derivatives, a working standard and a derivative blank were prepared for each batch to confirm the stability of derivatization and potential contamination during the derivatization process. Because it is impossible to obtain FCM samples free of all target chemicals, recoveries (n = 3) were calculated by subtracting background concentrations in nonsampled spikes from spiked samples. All FCMs were classified into five categories, including sugar-cane and reed-pulp fiber, grease-proof paper, polyethylene (PE)-coated greaseproof paper, aluminum-foil-coated paper and ivory board, and their corresponding FCMs, FCM6, FCM20, FCM55, FCM33, and FCM29 were chosen for recovery experiments, respectively. Spiked levels for the five FCMs were 300, 1, 1, 1, and 1 ng/g, respectively for each FTOH and 30, 1, 1, 1, and 1 ng/g, respectively for each PFCA (except for 2 ng/g PFOA for FCM33 and FCM29). The spiked concentrations were roughly 3–5 fold higher than concentrations in the FCMs. For food simulants, the spiked concentrations were 0.01 μg/L for FTOHs and 0.02 μg/L for PFCAs. Matrix effects for FCMS and food simulants were evaluated by adding FTOHs and PFCAs standards after sample preparation. For chemicals with detectable blank contamination, the MQLs were ten times the standard errors of procedural blanks, and final concentrations were calculated by the initial concentrations subtracting the mean blanks. For other chemicals, the MQLs were evaluated in matrix-spiked samples on the basis of the signal-to-noise ratio (S/N = 10) of the transition reaction used for quantification. To automatically correct for the loss of target compounds during sample preparation, potential matrix-induced changes to ionization, and for variations in instrumental response, we used a set of stable isotope labeled standards including 13C2-D2 PFBA, 13C4-PFHpDA, 13C2-PFTeDA, 13C4-PFHxTDA, 13C2-PPFPeA, 13C4-PPFPeDA, 13C4-PFPeDA, 13C2-D2-6:2 FTOH, 13C4-D2-8:2 FTOH, and 13C2-D2-10:2 FTOH as surrogate standards (Table S3). Calibration curves of standards of target analytes were calculated for derivatized FTOHs with a concentration series of 0.1, 0.5, 1, 5, 10, 50, 100, and 500 μg/L (except for 10:2 FTOH, which started with 0.02 μg/L) and for PFCAs with a concentration series of 0.1, 0.5, 1, 5, 10, 50, 100, and 250 μg/L (except for PFBA and PFPeA, which started with 0.2 μg/L). All calibration curves showed strong linearity (correlation coefficients >0.99) with good precision (RSD ≤ 5%). The signal-to-noise ratios for the lowest concentration on calibration curves of derivatized FTOHs and PFCAs were 13–32 and 10–19, respectively. Instrumental detection limits (IDLs) and instrumental quantification limits (IQLs) of analyzers were estimated based on S/N ratios of 3 and 10 of the transition reaction. Due to the lack of standards of 12:2 FTOH, 14:2 FTOH, 16:2 FTOH, and 18:2 FTOH, the four FTOHs derivatives were quantified using the standard curve of 10:2 FTOH derivative, as exemplified by the analysis of 12:2 FTOH and 14:2 FTOH in soil in a previous paper.21 and 13C2-D2-10:2 FTOH was used as the internal standard. Standards of perfluoropentadecanoic acid (PFPeDA) and perfluorohexadecanoic acid (PFHpDA) were also not commercially available, so concentrations of PFPeDA and PFHpDA were calculated using PFTeDA, as described in a previous study.22

Data Analysis. Statistical analysis was conducted using SPSS 19.0 (SPSS, Chicago, IL). For statistical analysis, concentrations below the MQL were substituted with a value equal to MQL/2. Significant differences among different materials were analyzed with a Kruskal–Wallis test.

RESULTS AND DISCUSSION

Identification of FTOHs in Food-Contact Materials. Although commercial standards of FTOHs can only be obtained for 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, some longer-chain FTOHs, such as 16:2 FTOH, have been suggested to exist in industrial products,23 and 12:2 FTOH has been widely observed in the atmosphere.24–26 To explore the potential occurrence of long-chain FTOHs in FCMs, we performed full-scan QTOF–MS analysis in positive-ion mode for the extracts of microwave popcorn bags after DNS derivatization. As shown in Figure 1, four peaks were observed when ions were extracted using theoretical masses of FTOH derivatives at m/z 898.0530 for 12:2 FTOH, 998.0466 for 14:2 FTOH, 1098.0402 for 16:2 FTOH, and 1198.0338 for 18:2 FTOH. The order of retention times of FTOH derivatives (6:2 FTOH < 8:2 FTOH < 10:2 FTOH < 12:2 FTOH < 14:2 FTOH < 16:2 FTOH < 18:2 FTOH) on a C18 column were consistent with their retention times of FTOH at 3.12, 3.37, and 3.62 min, respectively. The order of retention times of FTOH derivatives (6:2 FTOH < 8:2 FTOH < 10:2 FTOH < 12:2 FTOH < 14:2 FTOH < 16:2 FTOH < 18:2 FTOH) on a C18 column were consistent with their
molecular weight and predicted $K_{OW}$ values of native FTOHs.\textsuperscript{27} On the basis of the high-resolution MS\textsuperscript{1} spectra, we determined that the $m/z$ values for the four peaks were 898.0536, 998.0497, 1098.0406, and 1198.0328, with mass errors of 0.7, 3.1, 0.4, and −0.8 ppm, respectively (Table S2), compared with the theoretical $m/z$ values. The structures of the four peaks were further characterized by use of MS/MS mode of the QTOF−MS instrument. In the high-resolution MS\textsuperscript{2} spectra of the four peaks, the two most abundant fragment ions at $m/z$ 237 (237.0467) and $m/z$ 252 (252.0701) were observed, followed by $[\text{M}+\text{H}\cdot\text{CH}_3]^+$ (883.0298 for 12:2 FTOH, 983.0265 for 14:2 FTOH, 1083.0215 for 16:2 FTOH, 1183.0116 for 18:2 FTOH), $m/z$ 157 (157.0892) and $m/z$ 171 (171.1049) (Figure 2ab−d). None of the MS\textsuperscript{1} ions and MS\textsuperscript{2} fragment ions were detected in the DNS derivatization blank or in samples collected prior to derivatization, which indicated that the ions were dansylated derivatives of sample extracts (Figure S1). The predominant ion at $m/z$ 252 was governed by cleavage of the C−O bond, and further loss of a methyl group led to another predominant product ions at $m/z$ 237 (Figure 2b). These two predominant product ions at $m/z$ 252 and 237 were characteristic for FTOHs.\textsuperscript{20,29} To obtain more informative fragments from FTOHs, we used a MRM analysis in the negative-ion mode on a triple quadrupole instrument to characterize the nonderivatized FTOHs in extracts of microwave popcorn bags before DNS derivatization. Despite the relatively low sensitivity of the method to analyze nonderivatized FTOHs, four separated peaks at 4.62, 4.88, 5.08, and 5.23 min were observed for the predicted parent ions of $[\text{M}−\text{H}]^−$ (663 for 12:2 FTOH, 763 for 14:2 FTOH, 863 for 16:2 FTOH, and 963 for 18:2 FTOH) (Figure S2). A total of four diagnostic fragments that were generated by the loss of a set of HF and CO moieties were observed for all four peaks (Figure S3), which was consistent with those of shorter-chain FTOHs in this study and previously reported work.\textsuperscript{30} Thus, following multiple lines of evidence (relative retention time to known FTOHs, high-resolution MS\textsuperscript{1} spectra, high-resolution MS\textsuperscript{2} spectra, and MRM transitions prior to dansylation), the four peaks were identified as 12:2 FTOH, 14:2 FTOH, 16:2 FTOH, and 18:2 FTOH with a high degree of confidence. The identification of longer-chain FTOHs is significant because previous studies have shown that C\textsubscript{6−12} FTOHs can be biotransformed to the corresponding longer-chain C\textsubscript{7−11} PFCAs,\textsuperscript{31,32} and a recent study has highlighted the increasing temporal trend of longer-chain PFCAs in humans and wildlife.\textsuperscript{33}

**Validation of Analytical Method.** Considering the potentially low concentrations in various FCMs and the relatively low sensitivity in full scan QTOF−MS analysis, the quantification of FTOH derivatives and PFCAs in FCMs and food simulants were conducted using a triple-quadrupole instrument, and the analytical method was validated. The IDLs and IQLs of derivatized FTOHs were 0.004−0.007 and 0.013−0.023 μg/L, and those of PFCAs were 0.014−0.034 and 0.05−0.12 μg/L, respectively. The recoveries of FTOHs for the five categories of FCMs were 98−100%, 96−116%, 103−107%, 97−107%, and 86−109%, respectively (RSD ≤ 16%), and 66−92%, 82−97%, 83−94%, 78−95%, and 84−96%, respectively, for PFCAs (RSD ≤ 19%). For food simulants (water, ethanol−water, and oil), the recoveries of FTOHs and PFCAs were 68−86% (RSD ≤ 8%) and 76−109% (RSD ≤ 9%), respectively. Less than 17% signal suppression or enhancement was observed for all analytes in FCMs and food simulants. None of derivative blanks were observed for FTOHs in all batches of samples. PFHxA, 6:2 FTOH and 8:2 FTOH were detected in procedure blanks for FCMs (0.05 ± 0.02 ng/g for PFHxA, 0.23

![Figure 2. QTOF−MS/MS spectra of dansylated FTOHs with precursor ions of [M + H]^+ in extracts of food-contact materials at collision energy of 40−50 eV. (ab) 6:2 FTOH; (c) 8:2 FTOH; (d) 10:2 FTOH; (e) peak 1 (12:2 FTOH); (f) peak 2 (14:2 FTOH); (g) peak 3 (16:2 FTOH); (h) peak 4 (18:2 FTOH).](image-url)
± 0.06 ng/g for 6:2 FTOH, 0.13 ± 0.04 ng/g for 8:2 FTOH), and their MQLs were 0.20, 0.60, and 0.40 ng/g, respectively. The MQLs of 10:2 FTOH and other PFCAs in FCMs were 0.01 and 0.02–0.13 ng/g, respectively. The procedure blanks of PFHxS, 6:2 FTOH, and 8:2 FTOH for food simulants (water and ethanol–water) were 0.13 ± 0.50–0.15 ± 0.48, 2.73 ± 1.37–3.25 ± 1.42, and 2.57 ± 0.99–2.83 ± 1.08 ng/L, and their MQLs were 0.0048–0.0050, 0.0137–0.0142, and 0.0099–0.0108 μg/L, respectively. The MQLs of 10:2 FTOH and other PFCAs in food simulants (ethanol–water) were 0.00025 and 0.00025–0.000225 μg/L, respectively. 6:2 FTOH and 8:2 FTOH were detected in procedure blanks for oil with values of 4.64 ± 1.17 and 5.43 ± 2.91 ng/L, respectively. The MQLs of FTOHs and PFCAs in oil were 0.012 and 0.029 and 0.012–0.052 μg/L, respectively. The method recoveries and MDLs for FCMs and food simulants were shown in Table S4.

Concentrations of FTOHs and PFCAs in Food-Contact Materials from China. The concentrations of four newly identified long-chain FTOHs and three traditional shorter-chain FTOHs in FCMs made in China were investigated (Figure 3). All seven FTOHs were detected in 78% of FCMs (57/69) from China. Of the seven FTOHs, the median concentration of 8:2 FTOH (1.23 ng/g; <MQL−8490 ng/g) was the highest, followed by 10:2 FTOH (1.15 ng/g; <MQL−9350 ng/g), 12:2 FTOH (0.56 ng/g; <MQL−8450 ng/g), 6:2 FTOH (0.30 ng/g; <MQL−493 ng/g), 14:2 FTOH (0.15 ng/g; <MQL−1640 ng/g), 16:2 FTOH (<MQL; <MQL−372 ng/g), and 18:2 FTOH (<MQL; <MQL−130 ng/g) (Table 1). The total concentrations of the four longer-chain FTOHs (12:2 and longer, 944 ± 2110 ng/g) were comparable to those of the three traditional shorter-chain FTOHs (10:2 and shorter, 1480 ± 3640 ng/g). Detection frequencies of 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 14:2 FTOH, 16:2 FTOH, and 18:2 FTOH in FCMs were 38%, 65%, 77%, 70%, 58%, 35%, and 30%, respectively. Although 6:2 FTOH and 8:2 FTOH have been detected in microwave popcorn bags, this is the first report on the occurrence of 10:2 FTOH, 12:2 FTOH, 14:2 FTOH, 16:2 FTOH, and 18:2 FTOH in FCMs. Of the seven groups of FCMs, the concentrations of total FTOHs (ΣFTOHs) in microwave popcorn bags were up to 2620–24100 ng/g, which were much higher than that (<198 ng/g) reported previously. It should be noted that although relatively high concentration was also observed in paper tableware (median: 2990 ng/g, <MQL, 9070 ng/g), the high residuals in paper tableware, which was more widely used in China compared with popcorn bags, have not received enough attentions. Concentrations of ΣFTOHs in all other groups of FCMs, except FCM62 (cardboard for dry bread slices, 1230 ng/g), were lower than those in paper tableware and microwave popcorn bags, with concentrations that ranged from <MQL to 39 ng/g. It was further discovered that residuals of FTOHs in FCMs were largely dependent on the raw material and coating: the median concentrations of FTOHs in FCMs made of sugar cane and reed pulp fiber (2990 ng/g) and paper for microwave popcorn (18 200 ng/g) were significantly higher (p < 0.001) than those of other materials (1.68 ng/g for PE-coated greaseproof paper, 3.98 ng/g for aluminum-foil-coated paper, < MQL ng/g for uncoated greaseproof paper, and <MQL ng/g for ivory board) (Figure S4), which may be due to the inherently poor water- and oil-proofing properties of these raw materials. It should be noted that the concentration of total FTOHs in FCM16 (0.74 ng/g), which was composed of polystyrene and referred to as “EPS foam tableware”, was 13–12 600 times lower than concentrations of FTOHs in the eco-friendly paper tableware that was composed of plant fibers (9.36–9070 ng/g). EPS foam tableware has been widely used in snack bars and restaurants in China but was banned in 1999 due to its environmental persistence and the migration, at high temperatures, of the toxic monomer polystyrene into food. Since then, it has been replaced by eco-friendly biodegradable tableware such as paper materials made from plant fibers (sugar-cane and reed-pulp-fiber). The higher concentrations of FTOHs in eco-friendly paper tableware than in EPS foam tableware suggests that a comprehensive assessment of the eco-friendliness of FCMs and health risks of multiple chemicals in FCMs is necessary when formulating policy regarding the use of consumer products.

For comparison, residuals of PFCAs were also determined in FCMs from China (Figure 3). The median total concentration of PFCAs (2.95 ng/g) was lower than that of FTOHs (3.74 ng/g). Of the 15 detected PFCAs, PFOA was the most frequently detected congener (90%) with the highest median concentration of 1.72 ng/g (<0.05–103 ng/g), which was higher than FCMs from Thailand (0.16–10 ng/g), but much lower than FCMs from the United States (300–1200 ng/g) and Spain (53–198 ng/g). The highest median concentration of ΣPFCAs was detected in paper tableware (119 ng/g), followed by microwave popcorn bags (112 ng/g), which had much higher concentrations than in other groups (ranging from <MQL to 33 ng/g) (Table S5).
Although the profile of FTOHs in different FCMs varied greatly (Figure S5), three general profiles were observed (Figure 4). Of the 57 detectable FCMs, 8:2 FTOH was predominant in 22 FCM samples with a contribution of 48.9 ± 18.5% to total FTOHs, followed by 10:2 FTOH (26.6 ± 11.8%), 12:2 FTOH (13.8 ± 8.8%), 14:2 FTOH (5.2 ± 4.7%), 6:2 FTOH (4.3 ± 5.6%), 16:2 FTOH (1.1 ± 1.8%), and 18:2 FTOH (0.2 ± 0.6%), as exemplified by the profile of FCM5 in Figure 4. The proportion of 8:2 FTOH (60.3 ± 14.0%) in the sum concentrations of 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH was lower ($p < 0.001$) than those (>70%) in aqueous firefighting foams (AFFF) and waterproofing agents, but similar to those in gas released from polyol-based surfactants (64.8%), Teflon Advanced Carpet Protector (54.9%), and to those in two acrylate-linked commercial FTOH-based polymers in the United States. In two FCMs (FCM4, a paper bowl; FCM19, a cupcake cup), the major component was 6:2 FTOH, with a contribution as high as 95.3 ± 6.7%, which was 2-fold higher than that in gas released from Zonyl FSO 100 and Zonyl FSE (two fluorinated surfactants, 56.3% and 48.8%). It should be noted that 10:2 FTOH (44.5 ± 14.2%) was the most abundant FTOH in 30 FCMs, followed by 12:2 FTOH (23.8 ± 13.2%), 8:2 FTOH (18.2 ± 13.3%), 14:2 FTOH (8.0 ± 7.3%), 16:2 FTOH (1.4 ± 1.9%), 6:2 FTOH (1.2 ± 4.6%), and 18:2 FTOH (0.3 ± 0.6%), as exemplified by the profile of FCM1 in Figure 4. Although such a profile dominated by 10:2 FTOH has been reported in sludge-applied soils, the relatively high contributions of long-chain FTOHs were attributed to their chemical properties (e.g., their lower water solubility and octanol-air partitioning). This study, for the first time, provided evidence that products dominated by 10:2 FTOH are used in industry. Increasing temporal trends of long-chain PFCAs have been well documented in human serum samples from North America, Europe, and East Asia, but the source of long-chain PFCAs remains unclear. As important precursors of PFCAs, FTOHs have been demonstrated to metabolize to PFCAs in human. The production of 10:2 FTOH proposed in this study would partly contribute to the increasing temporal trends of long-chain PFCAs in humans.

### Concentrations of FTOHs in Food-Contact Materials from the United States.

Considering the high residuals of FTOHs and PFCAs in eco-friendly paper tableware and microwave popcorn bags made in China, the occurrence of FTOHs and PFCAs in these two kinds of FCMs made in the

![Figure 4. Profiles of FTOHs in three typical samples including FCM4, FCM5, and FCM1.](image-url)
United States were further investigated to understand differences in usage of FTOHs between the two countries. Compared with the results from paper tableware made in China, only 6:2 FTOH was detected in the paper tableware made in the United States, with relatively low detection frequencies of 11%, and relatively low concentrations of <MQL—495 ng/g. Of the 19 paper tableware samples from the United States, the concentrations of FTOHs in the single eco-friendly paper tableware (U1, 499 ng/g for 6:2 FTOH) were much higher than in those samples made of ivory board and plastic (<MQL—2.97 ng/g), which was similar to trends in FCMs from China. All FTOHs except 18:2 FTOH were detected in microwave popcorn bags from the United States, with median concentrations of 485 ng/g for 6:2 FTOH, 1.36 ng/g for 8:2 FTOH, 0.73 ng/g for 10:2 FTOH, 0.55 ng/g for 12:2 FTOH, 0.12 ng/g for 14:2 FTOH, and <MQL for 16:2 FTOH, which were lower than that made in China (18 200 ng/g for ΣFTOHs). In contrast to the three typical profiles of FTOHs in FCMs from China, 6:2 FTOH (97.4 ± 6.8%) was the major component in all detectable FCMs from the United States. This comparison study suggested that usage of 10:2 FTOH and longer-chain FTOHs has been effectively reduced in the United States, likely due to the 2010 and 2015 PFOA stewardship programs, while 10:2 FTOH and longer-chain FTOHs are still used in China.

**Migration Characteristics of PFASs in Paper Tableware.** Migration of PFASs from FCMs into food or food simulants has received wide attention because of potential human exposure. Although FTOHs and PFAs were widely detected in FCMs, migration characteristics of these chemicals from FCMs into food simulants were unavailable until this study (except PFOA). To better understand potential human exposure to FTOHs and PFAs via FCMs, we performed migration tests using a paper bowl, FCMs, with the median detection concentrations of FTOHs and PFAs. Water was chosen as a simulant for liquid food, which was one of the major contacted food types for paper bowls. Ethanol solutions (ethanol/water, 10:90, 30:70, and 50:50) and oil were also included as food simulants for alcohol and lipids to explore the migration characteristics of FTOHs and PFAs. Of the 15 PFAs, 9 PFAs (C₄₋₁₂) were detected in 10 mL of water and 10% ethanol with amounts of 0.01–0.96 and 0.01–1.07 ng, 12 PFAs (C₆₋₁₄) were detected in 10 mL of 30% ethanol with amounts of 0.01–2.73 ng, and all PFAs were detected in 10 mL of 50% ethanol with amounts of 0.01–24.6 ng. None of PFAs were detected in 10 mL of oil, probably due to the relatively high MQLs or relatively low migration efficiencies. Migration efficiencies of PFAs from paper bowls into water ranging from 0.005% for PFDoDA to 18.3% for PFOA, depending on the carbon-chain lengths (Table 2). Compared with the results from water, migration efficiencies of PFAs into ethanol solutions significantly increased with the component ratio of ethanol: 0.034–18.1% for 10% ethanol, 0.010–21.4% for 30% ethanol, and 0.18–32.5% for 50% ethanol. The migration efficiency of PFOA (0.83–28.7%) in the present study was lower than in previous papers (e.g., 20–41% after sonication for 30 min at 100°C), which is likely due to the relatively shorter contact time and weaker contact conditions used in this study.

All FTOHs except 18:2 FTOH were detected in 10 mL of food simulants with amounts ranging from 0.01 to 370 ng. Similar to the results for PFAs, migration efficiencies of FTOHs into water and 10% ethanol simulant were dependent on their carbon-chain lengths, ranging from 0.004% for 16:2 FTOH to 0.24% for 6:2 FTOH. The component ratios of ethanol in food simulants were also an important factor for the migration efficiencies of FTOHs from FCMs, and migration efficiencies increased to 0.009–2.79% for 30% ethanol and 0.06–13.0% for 50% ethanol. The migration efficiencies of FTOHs into oil ranged from 0.04% (16:2 FTOH) to 2.28% (8:2 FTOH), similar to those into 30% ethanol.

Overall, in addition to PFAs, FTOHs were widely detected in various paper-made FCMs, especially in eco-friendly paper tableware and microwave popcorn bags, and long-chain...
FTOHs (12:2 FTOH, 14:2 FTOH, 16:2 FTOH, and 18:2 FTOH) were, for the first time, characterized in consumer products. This study proposed that humans were not only exposed to FTOHs and PFCAs via drinking water or air but also via the ingestion of food products to which FTOHs and PFCAs had migrated from FCMs. The present work provides important information for comprehensively understanding human exposure to PFCAs and FTOHs.

**ASSOCIATED CONTENT**

1. **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03806.

Text, figures, and tables addressing chemicals and reagents; UPLC–ESI–MS/MS analysis; UPLC–QTOF–MS analysis; detailed information of food-contact materials; precursors and MS/MS fragment ions (UPLC–QTOF–MS) of FTOHs derivatized with dansyl chloride in paper-made FCMs; multiple reaction monitoring (MRM) transitions and mass spectrometry parameters of FTOHs and PFCAs in a triple quadrupole instrument; recoveries and method-detection limits (MQLs) of FTOHs and PFCAs for different categories of FCMs and food simulants; median concentrations (ng/g) and ranges of PFCAs in food-contact materials made in China; QTOF–MS/MS spectra of dansylated FTOHs with precursor ions of [M + H]+ in DNA derivatization blank at collision energy of 40–50 eV; chromatograms of FTOHs in food-contact materials before and after derivatization, generated from UPLC–ESI–MS/MS; chromatograms of nonderivatized FTOHs in food-contact materials, generated from UPLC–ESI(−)–MS/MS by multiple reaction monitoring (MRM); comparison of total concentrations of PFCAs and FTOHs among different materials from China; profiles of individual FTOHs in different FCMs made in China; and typical UPLC–MS chromatograms of PFCAs in food-contact materials. (PDF)

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Notes

The authors declare no competing financial interest.

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