Determination of fluorotelomer alcohols and their degradation products in biosolids-amended soils and plants using ultra-high performance liquid chromatography tandem mass spectrometry

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ABSTRACT

Degradation of fluorotelomer alcohols (FTOHs) was recognized as an additional source of perfluorocarboxylic acids (PFCAs). Quantification of FTOHs and their degradation products can help shed light on the sources and fates of PFCAs in the environment. In this study, an analytical method was developed for the determination of 6:2 and 8:2 FTOHs, and their degradation products of poly- and perfluorinated acids, including fluorotelomer saturated and unsaturated carboxylic acids (FTCAs and FTUCAs), secondary polyfluorinated alcohols and PFCAs in biosolids-amended soils and plants using ultra-high performance liquid chromatography tandem mass spectrometry (UPLC–MS/MS). The extract efficiencies of different methods including ethyl acetate and methanol (MeOH) for FTOHs and acetonitrile, MeOH, methyl tert-butyl ether (MTBE), NaOH–MeOH and NaOH–MTBE for poly- and perfluorinated acids were tested. The results showed that 6:2 and 8:2 FTOHs and their degradation products could be simultaneously and satisfactorily extracted by MeOH, cleaned up by Envi-Carb graphitized carbon and solid phase extraction, respectively, and determined by UPLC–MS/MS separately. NaOH in the extractant caused the conversion of 6:2 FTCA and 8:2 FTCA into the corresponding FTUCAs. The selected methods have matrix recoveries ranged from 52% to 102%, and detection limits of 0.01–0.46 ng/g dry weight for FTOHs and their degradation products in soil and plant. The optimized method was applied successfully to quantify FTOHs and their degradation products in two biosolids-amended soils and plants. The total concentrations of FTOHs in the soils were 44.1 ± 5.8 and 82.6 ± 7.1 ng/g, and in plants tissues 3.58 ± 0.25 and 8.33 ± 0.66 ng/g. The total concentrations of poly- and perfluorinated acids in the soils were 168.0 ± 13.2 and 349.6 ± 11.2 ng/g, and in plants tissues 78.0 ± 6.4 and 75.5 ± 5.3 ng/g.

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1. Introduction

Perfluoroalkyl acids (PFAAs), including perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs), have been manufactured and used for more than 60 years. They are employed in materials such as surfactants, lubricants, varnishes, pesticides and fire retardant foams, the subsequent disposal of which results in the wide detection of these compounds in various environmental media [1–4] and biological species [5–7]. Because of their ubiquitous occurrence, environmental persistence [8], bioaccumulation

[9] and potential toxicity [10], PFAAs have raised serious concerns. PFAAs may enter the environment through direct manufacturing emissions, releasing from products during their use and disposal, as well as through indirect precursor transformation [11]. With effective reduction in release from direct sources in recent years, exploring the indirect sources of PFAAs has become increasingly important [11–13].

As raw materials used to produce fluoropolymers and fluorosurfactants, fluorotelomer alcohols (FTOHs) are applied in a variety of industry and households [14]. Degradation of FTOHs has been recognized as an additional source of PFCAs in the environment [11]. Substantial information is available on abiotic [15–17] and biotic [18–23] degradation of FTOHs under laboratory conditions. Ellis et al. [15] reported FTOHs could be degraded in the

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atmosphere to yield a homologous series of PFCAs through peroxy radical cross reactions. Brandsma et al. [23] found that fluorotelomer saturated carboxylic acids (FTCAs) and fluorotelomer unsaturated carboxylic acids (FTUCAs) were the major products detected in rainbow trout following dietary exposure to FTOHs. Biodegradation of 8:2 FTOH in aerobic soils shared common pathways as those reported in aerobic activated sludge, mixed bacterial culture and mammalian metabolism, which proceeded via saturated and unsaturated fluorotelomer carboxylic acid intermediates [18]. In these studies, different degradation intermediates of FTOHs, such as poly- and perfluorinated acids, fluorotelomer aldehydes and secondary polyfluorinated alcohols, and terminal degradation products of PFCAs were identified, which helped unveil the degradation pathway of FTOHs, and further deduced the source of PFCAs in the environment.

Sewage sludge generated in wastewater treatment plants (WWTPs) is widely considered as an important sink of PFAAs and their precursors [24–26]. Land application of treated sewage sludge (biosolids) may release PFAAs and their precursors into the soils [27–29]. Yoo et al. [27] and Washington et al. [29] reported the accumulation of PFAAs and FTOHs in soils as a result of land use of biosolids from industrial sources. These compounds in the contaminated soils may enter into the food chain by plant uptake and exert a potential health risk. Yoo et al. [7] optimized extraction methods to quantify PFAAs and FTOHs in plants from biosolids-amended fields using liquid chromatography/tandem mass spectrometry (LC/MS/MS) and gas chromatography/mass spectrometry (GC/MS), respectively. Wen et al. [30] determined the accumulation of PFAAs in wheat (*Triticum aestivum* L.) grown in biosolids-amended soils. However, information about the degradation of FTOHs in biosolids-amended soils and plants under field condition is limited.

To evaluate the risks of PFAAs following biosolids land application, the degradability of precursors should be taken into account. Thus, it is essential to establish fast and reliable analytical methods for precursors and their intermediates and terminal metabolites in biosolids-amended soils and plants. While there are a number of peer-reviewed publications reporting extraction methods for PFAAs and FTOHs in solid and biological matrices [28,31–34], methodological studies on the extraction of FTOHs and their degradation products from plants are limited. In this study, the efficiency of different extractants, which have been reported for extracting PFAAs and FTOHs from solid and biological samples [7,26,30,35–37], including acetonitrile (ACN), methanol (MeOH), methyl tert-butyl ether (MTBE), NaOH–MeOH and NaOH–MTBE for the extraction of FTOHs degradation products of poly- and perfluorinated acids, and ethyl acetate (EtOAc) and MeOH for the extraction of FTOHs, was tested. The results showed that both FTOHs and their degradation products of poly-perfluorinated acids could be extracted by MeOH efficiently. The extracts were then subjected to cleanup prior to determination using ultra-high performance liquid chromatography tandem mass spectrometry (UPLC–MS/MS). The optimized method was then applied to the determination of two widely used FTOHs, 6:2 and 8:2 FTOHs [20], and their degradation products in biosolids-amended field soil and plant samples. To the best of our knowledge, this is the first report to extract FTOHs and their degradation products simultaneously in soils and plants sampled from biosolids-amended field and determine the analytes using UPLC–MS/MS.

2. Materials and methods

2.1. Reagents and standards

Three FTOHs and 13 poly- and perfluorinated acids, including six PFCAs, five FTCAs and two FTUCAs were examined in this

study (Table 1). Purities of all the analytical standards were $\geq 97\%$. 6:2 FTOH and 8:2 FTOH were purchased from Matrix Scientific (Columbia, SC, USA). PFBA, PFPeA, PFHxA and PFHpA were from J&K Scientific Ltd. (Beijing, China). PFOA was from Strem Chemicals Inc. (Newburyport, MA, USA). PFNA was from Alfa Aesar (Ward Hill, MA, USA). 4:3 FTCA and 7:3 FTCA were from Apollo Scientific Ltd. (Bredbury, UK). 5:3 FTCA, 6:2 FTUCA, 6:2 FTCA, 8:2 FTUCA, 8:2 FTCA, 7:2 sFTOH and stable isotope-labeled standards M6:2 FTOH, M8:2 FTOH, MPFBA, MPFHxA, MPFOA, MPFNA, M6:2 FTUCA, M6:2 FTCA, M8:2 FTUCA, M8:2 FTCA were from Wellington Laboratories Inc. (Guelph, Ontario, Canada).

All reagents were of analytical reagent grade or better. Tetra-butyl ammonium hydrogen sulfate (TBAHS), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), ethanolamine and acetic acid (CH_3COOH) were purchased from Sigma–Aldrich Chemical (Milwaukee, WI, USA). Weak anion exchange (Oasis® WAX, 6 cm^3 , 150 mg , $30\text{ }\mu\text{m}$) solid phase extraction (WAX–SPE) cartridges were purchased from Waters Corp. (Milford, MA, USA). Supelclean graphitized carbon (ENVI–Carb) was obtained from Supelco Inc. (Bellefonte, PA, USA). ACN, MeOH and MTBE (Fisher Chemical, Fairlawn, NJ, USA) were of HPLC grade. Purified water obtained by a Milli-Q Synthesis water purification system (Millipore, Bedford, MA, USA) was used throughout the experiment.

Reference standards solutions of three FTOHs, 13 poly- and perfluorinated acids, and isotope labeled internal standards were made in MeOH, stored in sealed glass containers, and put into -20°C refrigerators.

2.2. Soil and plant samples

Explorative evaluations were performed using uncontaminated soils and maize plants (blanks) collected from an experimental field at Beijing Academy of Agriculture and Forestry Sciences. After the optimization process was completed, the established method was used to determine FTOHs and poly- and perfluorinated acids concentrations in biosolids-amended soils and plants. Two soil samples and two maize plant samples were collected from biosolids-amended agricultural fields in Dezhou, Shandong province, China ($37^\circ 20'\text{N}$, $116^\circ 38'\text{E}$) in September 2013. Soil samples were taken from the cultivated surface layer (0–20 cm), freeze-dried, ground, and screened through a MeOH-washed, 2 mm stainless-steel sieve to remove large particles. The selected soil properties are given in Table S1 in the Supplementary materials.

Plant samples were divided into roots, stems and leaves. The subsamples of maize were washed thoroughly with tap water and Milli-Q water sequentially, freeze-dried and ground. All dried samples were stored at -20°C before analysis.

2.3. Selection of extractants for FTOHs and Envi-Carb graphitized carbon cleanup

To evaluate the extraction efficiency of EtOAc and MeOH, recovery tests for 6:2 FTOH, 7:2 sFTOH and 8:2 FTOH in soils and plant roots and shoots were conducted. Two grams of blank soils or 0.5 g blank plant tissues were weighed in 15 mL polypropylene (PP) centrifuge tubes. Before extraction, $50\text{ }\mu\text{L}$ of 6:2 FTOH, 7:2 sFTOH and 8:2 FTOH mixture solutions (200 ng/mL for each analyte in MeOH) were added and aged for 24 h.

All samples were extracted by EtOAc according to the method of Yoo et al. [7] with some modifications. Briefly, 5 mL of water and 5 mL of EtOAc were added to the samples sequentially and mixed. The samples were then kept in a constant-temperature shaker (ZWY-210, Shanghai Zhicheng Analytical Instrument Manufacturing Co., Ltd., Shanghai, China) at 25°C for extraction. After 8 h, the samples were centrifuged ($2686 \times g$, 20 min) to consolidate the EtOAc fraction. This extraction step was repeated twice. All organic

Table 1
List of target compounds analyzed, and the MS/MS parameters used.

Acronym	Chemical name	CAS registry number	Formula	Quantitation transition (<i>m/z</i>)	Cone voltage (V)	Collision energy (eV)
6:2 FTOH	6:2 fluorotelomer alcohol	647-42-7	F(CF ₂) ₆ CH ₂ CH ₂ OH	362.97 > 255.04	12	28
7:2 sFTOH	7:2 secondary polyfluorinated alcohol	24015-83-6	F(CF ₂) ₇ CHOHCH ₃	393.00 > 219.00	20	15
8:2 FTOH	8:2 fluorotelomer alcohol	678-39-7	F(CF ₂) ₈ CH ₂ CH ₂ OH	462.97 > 355.00	14	18
PFBA	Perfluorobutyric acid	375-22-4	F(CF ₂) ₃ COOH	212.97 > 169.03	16	8
PFPeA	Perfluoropentanoic acid	2706-90-3	F(CF ₂) ₄ COOH	262.97 > 219.03	14	6
PFHxA	Perfluorohexanoic acid	307-24-4	F(CF ₂) ₅ COOH	312.97 > 269.03	12	12
PFHpA	Perfluoroheptanoic acid	375-85-9	F(CF ₂) ₆ COOH	362.97 > 319.04	14	12
PFOA	Perfluorooctanoic acid	335-67-1	F(CF ₂) ₇ COOH	412.97 > 368.97	16	8
PFNA	Perfluorononanoic acid	375-95-1	F(CF ₂) ₈ COOH	462.97 > 419.04	14	8
4:3 FTCA	4:3 polyfluorinated acid	80705-13-1	F(CF ₂) ₄ CH ₂ CH ₂ COOH	291.03 > 187.03	18	12
5:3 FTCA	5:3 polyfluorinated acid	914637-49-3	F(CF ₂) ₅ CH ₂ CH ₂ COOH	340.97 > 237.03	18	12
7:3 FTCA	7:3 polyfluorinated acid	812-70-4	F(CF ₂) ₇ CH ₂ CH ₂ COOH	441.03 > 337.04	22	14
6:2 FTUCA	6:2 fluorotelomer unsaturated carboxylic acid	70887-88-6	F(CF ₂) ₅ CF=CHCOOH	356.97 > 293.01	14	16
6:2 FTCA	6:2 fluorotelomer saturated carboxylic acid	53826-12-3	F(CF ₂) ₆ CH ₂ COOH	376.97 > 292.99	14	22
8:2 FTUCA	8:2 fluorotelomer unsaturated carboxylic acid	70887-84-2	F(CF ₂) ₇ CF=CHCOOH	456.97 > 393.02	16	12
8:2 FTCA	8:2 fluorotelomer saturated carboxylic acid	27854-31-5	F(CF ₂) ₈ CH ₂ COOH	476.97 > 393.05	14	22
Mass-labeled analytes						
M6:2 FTOH	[1,1-D ₂ ,1,2- ¹³ C ₂] 6:2 FTOH	N.A. ^a	F(CF ₂) ₆ ¹³ CH ₂ ¹³ CD ₂ OH	367.03 > 256.01	12	18
M8:2 FTOH	[1,1-D ₂ ,1,2- ¹³ C ₂] 8:2 FTOH	N.A.	F(CF ₂) ₈ ¹³ CH ₂ ¹³ CD ₂ OH	467.03 > 356.02	12	22
MPFBA	¹³ C ₄ -PFBA	N.A.	F(¹³ CF ₂) ₃ ¹³ COOH	216.97 > 172.05	14	8
MPFHxA	¹³ C ₅ -PFHxA	N.A.	F(CF ₂) ₄ ¹³ CF ₂ ¹³ COOH	314.97 > 270.05	14	8
MPFOA	¹³ C ₄ -PFOA	N.A.	F(CF ₂) ₄ (¹³ CF ₂) ₃ ¹³ COOH	416.97 > 372.06	14	10
MPFNA	¹³ C ₅ -PFNA	N.A.	F(CF ₂) ₄ (¹³ CF ₂) ₄ ¹³ COOH	467.97 > 423.00	16	6
M6:2 FTUCA	¹³ C ₂ -6:2 FTUCA	N.A.	F(CF ₂) ₅ CF=CH ¹³ COOH	358.97 > 294.04	16	14
M6:2 FTCA	¹³ C ₂ -6:2 FTCA	N.A.	F(CF ₂) ₆ ¹³ CH ₂ ¹³ COOH	379.03 > 294.02	14	14
M8:2 FTUCA	¹³ C ₂ -8:2 FTUCA	N.A.	F(CF ₂) ₇ CF=CH ¹³ COOH	458.97 > 394.05	18	18
M8:2 FTCA	¹³ C ₂ -8:2 FTCA	N.A.	F(CF ₂) ₈ ¹³ CH ₂ ¹³ COOH	478.97 > 394.05	14	22

^a N.A., not available.

supernatants of the extractions were combined and allowed to evaporate under a gentle stream of nitrogen to 500 μ L. Then the concentrated extractions were mixed with 500 μ L MeOH before cleanup.

For MeOH extraction, 6 mL of MeOH were added to the samples. After mixing and shaking for 8 h, the MeOH were separated by centrifugation (2686 $\times$ g, 20 min) and transferred to a second PP tube. The samples were then extracted twice with 2 $\times$ 6 mL solvents. All organic supernatants were combined and allowed to evaporate to 1.0 mL under nitrogen before being cleaned by Envi-Carb graphitized carbon.

All extractions were performed in quadruplicate. The extracts were cleaned up by Envi-Carb graphitized carbon as reported by Ruan et al. [38] with some modifications. Briefly, a 500 μ L aliquot of the extract was placed into a 2 mL disposable PP microcentrifuge tube, which contained 20 mg Envi-Carb graphitized carbon that was treated with 40 μ L of 0.1 M NaOH. The tube was capped and vortexed for 1 min, then centrifuged at 8600 $\times$ g for 30 min. The supernatant was gathered before UPLC–MS/MS analysis.

2.4. Selection of extractants for poly- and perfluorinated acids and SPE cleanup

Studies have shown ACN [35], MeOH [26], MTBE [36], NaOH–MeOH [37], NaOH–MTBE [30] are efficient in the extraction of PFAAs from environmental samples. To evaluate the capacity of different solvents, recovery tests for FTOH degradation products of poly- and perfluorinated acids in soils and plant roots and shoots were conducted. Two grams of blank soils or 0.5 g blank plant tissues were weighed in 15 mL PP centrifuge tubes. Before extraction, 50 μ L of

poly- and perfluorinated acids mixture solutions (200 ng/mL for each analyte in MeOH) were added and aged for 24 h.

For the extraction by MTBE and NaOH–MTBE, all samples were extracted according to the methods of Hansen et al. [36] and Vestergren et al. [31], respectively, with some modifications. Briefly, 1.5 mL of water (or 0.4 M NaOH solution) was added to the tube. After mixing for 30 min, 2 mL of 0.25 M Na₂CO₃/NaHCO₃ buffer and 1 mL of 0.5 M TBAHS solution were added. After thorough mixing, 5 mL of MTBE was added to the solution. The mixture was shaken for 8 h, and then centrifuged (2686 $\times$ g) for 20 min. The organic and aqueous layers were separated by centrifugation, and MTBE was transferred to a second PP tube. The aqueous mixture was extracted twice with 2 $\times$ 5 mL MTBE. All organic supernatants of the three extractions were combined, evaporated to dryness under a gentle stream of nitrogen, and then reconstituted in 1.0 mL of MeOH before SPE cleanup.

For the extraction by ACN, MeOH, or 0.05 M NaOH in MeOH (NaOH/MeOH), 6 mL of solvents were added to the samples. After mixing and shaking for 8 h, the solvents were separated by centrifugation (2686 $\times$ g, 20 min) and then transferred to a second PP tube. The samples were extracted twice with 2 $\times$ 6 mL solvents. All organic supernatants of the three extractions were combined and allowed to evaporate under nitrogen to 1.0 mL prior to SPE cleanup.

All extractions were performed in quadruplicate. Clean-up of the extracts were by Oasis WAX cartridges as reported by Taniyasu et al. [39] with some modifications. All the extracts were diluted with 30 mL milli-Q water (the solution pH was adjusted to 6 with HCl solution for NaOH–MeOH extraction). Before SPE cleanup, the samples were filtered using a 0.45 μ m nylon filter (Nylon 66, Tianjin Navigator Lab Instrument Co., Ltd, Tianjin, China) and then passed

through cartridges pre-conditioned with 4 mL of 0.1% ammonium hydroxide in MeOH and 4 mL of Milli-Q water sequentially. The cartridges were then washed with 25 mM sodium acetate buffer solution (pH 4) and dried completely under vacuum. The target compounds were eluted by 4 mL of 0.1% ammonium hydroxide in MeOH. The elution was concentrated to 1.0 mL under a nitrogen stream. The final extraction was centrifuged ($8600 \times g$) to remove particles before injection to UPLC–MS/MS.

2.5. Effects of NaOH concentrations on 6:2 FTCA and 8:2 FTCA conversions

The effects of NaOH concentrations on the conversions of 6:2 FTCA and 8:2 FTCA were determined. Briefly, 50 mL of 50 ng/mL 6:2 FTCA (or 8:2 FTCA) was prepared in 0.01 M NaOH/MeOH and 0.05 M NaOH/MeOH, with continuous shaking on a rotary shaker (25 °C) at 125 rpm. At increasing time intervals (1, 3, 5, 7, 12 and 24 h), 0.5 mL solution was removed and neutralized with HCl immediately. The concentrations of 6:2 FTCA and 6:2 FTUCA (or 8:2 FTCA and 8:2 FTUCA) in the solution were determined using UPLC–MS/MS. Fifty ng/mL 6:2 FTCA (or 8:2 FTCA) in MeOH without NaOH was used as control. The experiments were repeated two times.

2.6. Instrumental analysis and quantification

The purified sample extracts were analyzed using a Waters ultra-performance liquid chromatography (UPLC) system coupled to a Xevo TQS tandem mass spectrometer (MS/MS) with an electrospray ionization (ESI) interface. The separation of the FTOHs was achieved on a BEH Shield RP18 column (1.7 μ m particles, 150 mm $\times$ 2.1 mm, Waters) with a 1 mM ethanolamine in water/MeOH gradient mobile phase at a flow rate of 0.15 mL/min. MeOH was initialized at 50%, then ramped to 85% in 1.0 min and held for 5.0 min, and ramped back to 50% in 0.5 min and held for 3.5 min. Column temperature was maintained at 35 °C. The FTOHs degradation products of poly- and perfluorinated acids were separated through a BEH C18 column (1.7 μ m particles, 50 mm $\times$ 2.1 mm, Waters) with column temperature setting at 35 °C. A binary gradient elution program was applied with a constant flow rate of 0.4 mL/min. The mobile phase consisted of solvent (A) ACN and (B) 0.15% acetic acid in water, with an initial gradient of 5% A. At 2.5 min, the gradient increased to 60% A and held until 4.0 min, then linearly reverted to original conditions at 4.5 min. The column was reconditioned for 1.5 min at the starting composition of 5% A prior to the next injection.

Five microliters of solution was injected. The ESI source was operated in the negative ion mode with a capillary voltage of 3.0 kV, source temperature of 120 °C for FTOHs, and 150 °C for poly- and perfluorinated acids. Nitrogen was used as desolvation gas (flow rate 600 L/h, temperature 350 °C) and as cone gas (flow rate 50 L/h). Argon was used as collision gas at a flow rate of 0.15 mL/min. The detection was performed by ESI–MS/MS analyses using the multiple reaction mode (MRM) by measuring the transition of the precursor ion $\rightarrow$ product ion for FTOHs and its metabolic products. Cone voltages and collision energies were optimized for each analyte to obtain the highest sensitivity and resolution. MS/MS parameters for the analytes including their quantitation transitions, cone voltages, and collision energies are listed in Table 1. The MassLynx Software v.4.1 (Waters) was used for instrument control, data acquisition and processing.

2.7. Determination of FTOHs and their degradation products in biosolid-amended soils and plant tissues

Before extraction, 10 isotope labeled internal standards were spiked (5 ng of each standard) to 2 g of biosolids-amended soils or

Fig. 1. Flow-chart of analytical method for FTOHs and poly- and perfluorinated acids in soil and plant samples.

0.5 g of plants and aged for 24 h. 6:2 FTOH, 8:2 FTOH and their degradation products of secondary polyfluorinated alcohols and poly- and perfluorinated acids in soil and plant samples were extracted by MeOH simultaneously according to the methods described above. The MeOH extract was evaporated to 1.0 mL. Half of the extract (0.5 mL) was subjected to Envi-Carb graphitized carbon cleanup for FTOHs analysis as described in Section 2.3. The other 0.5 mL extract was diluted with Milli-Q water to a final volume of 15 mL and subject to WAX-SPE cleanup for poly- and perfluorinated acids analysis as described in Section 2.4. The FTOHs and poly- and perfluorinated acids in purified sample extracts were analyzed by UPLC–MS/MS using BEH Shield RP18 and BEH C18 columns, respectively. The analytical procedure is shown by the flow chart in Fig. 1.

Matrix calibration curves using spiked uncontaminated samples that were extracted in analogy to the samples were applied for quantification. A seven point calibration curve ranging for all target analytes from 0.5 to 100 ng/g was performed at the beginning and at the end of every sample batch. Linear regression analysis was performed by plotting the peak area of the analyte over the analyte concentration, and the fitted lines had correlation coefficients (*R*) values of at least 0.997 for all compounds. Recoveries were determined by comparing matrix-free direct injections of the same amount of spiked ^{13}C internal standards with ^{13}C spiked blank extracts and ^{13}C spiked samples. Compounds with no isotope labeled standard were corrected with the closest available internal standard, though this correction may lead to possible bias.

The limits of detection (LODs) and quantification (LOQs) for FTOHs and poly- and perfluorinated acids were defined as the concentration corresponding to the mean peak area plus three standard deviations ($\bar{x} + 3 \times \sigma$) or plus 10 standard deviations ($\bar{x} + 10 \times \sigma$) of extracts from the uncontaminated soils or plant tissues. The LODs and LOQs were measured for each matrix on replicate analyses ($n = 7$) of uncontaminated samples.

3. Results and discussion

3.1. Chromatograms of FTOHs and poly- and perfluorinated acids

The separation of the FTOHs and their degradation products of poly- and perfluorinated acids were achieved on a ACQUITY UPLC BEH Shield RP18 column (1.7 μ m particles, 150 mm $\times$ 2.1 mm, Waters), and a ACQUITY UPLC BEH C18 column (1.7 μ m particles, 50 mm $\times$ 2.1 mm, Waters), respectively. The later one is a trifunctionally bonded alkyl column, which can impact the retention, selectivity and sensitivity of ionizable compounds, thus has been used to separate PFAAs extensively [7,30,31,33]. The former one contains an embedded-polar group that combines the hydrophobicity of a straight-chain-alkyl ligand (C18) with the hydrophilicity of an embedded polar group (carbamate), which improves the retention of and peak shape of polyhydric substances [40,41]. Two ACQUITY UPLC BEH Shield RP18 columns with different lengths (50 mm $\times$ 2.1 mm and 150 mm $\times$ 2.1 mm) were compared and it was found that the longer column (150 mm $\times$ 2.1 mm) had both higher separation efficiency and better peak shape.

The mass chromatograms of FTOHs and poly- and perfluorinated acids are shown in Fig. 2(a) and (b), respectively. Baseline separation was achieved within 6 min and 4.2 min for FTOHs and poly- and perfluorinated acids, respectively, except for 5:3 and 6:2 FTCA. GC/MS has been routinely used to analyze FTOHs in environmental samples [27,42,43], with analytical time for 6:2 FTOH, 7:2 sFTOH and 8:2 FTOH ranged 8.5–12 min, about 1.4–2.0 times longer than our method. LC/MS/MS is widely utilized for the quantification of FTOHs degradation products [18,19,21–23]. The analytical time of eight degradation products (PFPeA, PFHxA, PFHpA, PFOA, PFNA, 7:3 FTCA, 8:2 FTUCA and 8:2 FTCA) reported was about 9.5 min [21], which were 2.3 times longer than our method. The fast analyses for both FTOHs and their degradation products obtained in this study suggested the effectiveness of UPLC–MS/MS separation.

3.2. Selection of analysis method for FTOHs

FTOHs in soil and plant tissues were extracted by EtOAc and MeOH and cleaned by Envi-Carb graphitized carbon. The results are shown in Table S2 in the Supplementary materials. EtOAc extraction was reported to have greater yields of FTOHs from plants than MTBE and dichloromethane did [7]. Results from this study showed that MeOH extractions gave satisfactory recoveries of 87–102%, with relative standards deviations (RSDs) based on four replicate analyses at 4.5–7.4%. These values were equivalent to those of EtOAc extraction, whose recoveries were in the range of 89–101%, and RSDs were 3.2–9.5%. However, EtOAc is not suitable to inject into UPLC–MS/MS directly, MeOH was thus used in the following study.

The extracted supernatants were cleaned up with graphitized carbon adsorbent to remove natural organic matters that are likely to cause matrix interference in the mass spectrometer. Addition of glacial acetic acid to graphitized carbon was used to saturate the ion exchange sites on the sorbents [44]. However, the acetic acid present could form adduct with FTOHs and suppress their ionization. Liu et al. [45] suggested that the water in 90% ACN/10% NaOH solvent extract was sufficient to saturate the ion exchange site during the analysis of soil samples. Ruan et al. [38] used Envi-Carb graphitized carbon added with 1 M NaOH to clean up 6:2 fluorotelomer iodide and its degradation products in soil extracts. Therefore, graphitized carbon was treated with NaOH solution for FTOH cleanup in this experiment. We also tested the effectiveness of WAX-SPE for FTOHs cleanup following MeOH extraction, according to Taniyasu et al. [39]. We found that the recoveries of 6:2 FTOH, 7:2 sFTOH and 8:2 FTOH in soil and plant matrices after MeOH

Fig. 2. Mass chromatograms of FTOHs (a) and poly- and perfluorinated acids (b) in standard mixture (5 ng/mL).

extraction and WAX-SPE cleanup were less than 60% (Table S3 in the Supplementary materials) which were much lower than Envi-Carb graphitized carbon cleanup. Therefore, WAX-SPE was not used for FTOHs cleanup in the following experiment.

Fig. 3. Recoveries of spiked poly- and perfluorinated acids in soil (a), root (b) and shoot (c) by different solvents followed by WAX-SPE cleanup.

3.3. Selection of extractants for poly- and perfluorinated acids analysis

The methods available for biota analysis of PFAAs are mostly based on three extraction procedures: ion pair extraction, solvent

liquid extraction, and alkaline digestion [34]. In this study, the extraction accuracy and precision of five solvents, ACN, MeOH, MTBE, NaOH-MeOH, and NaOH-MTBE coupled with WAX-SPE cleanup were compared. The results are shown in Fig. 3. The extraction recoveries for ACN were in the range of 11–59% for soils and

Fig. 4. Conversion kinetics of 50 ng/mL 6:2 FTCA and 8:2 FTCA in 0.01 M and 0.05 M NaOH/MeOH.

54–102% for plant tissues, which suggested that ACN is not suitable to extract poly- and perfluorinated acids from soils. MeOH and MTBE had similar extraction capacities, with the recoveries ranged 77–102% and 57–103%, respectively, for PFCAs, 52–75 and 51–85%, respectively for FTCAs, and 74–95 and 57–85%, respectively, for FTUCAs. The RSDs of MeOH method (1.9–10.8%) was relatively smaller than those of MTBE method (4.1–14.5%). The extraction capacities of NaOH-MeOH and NaOH-MTBE were equivalent to those of MeOH and MTBE for PFCAs, 18–39% higher than those of MeOH and MTBE for 4:3 FTCA, 5:3 FTCA and 7:3 FTCA. However, the recoveries of NaOH-MeOH and NaOH-MTBE extraction for 6:2 FTCA and 8:2 FTCA were less than 46%, while those for 6:2 FTUCA and 8:2 FTUCA were higher than 147%, suggesting the underestimation of 6:2 FTCA and 8:2 FTCA, and overestimation of 6:2 FTUCA and 8:2 FTUCA when NaOH-MeOH and NaOH-MTBE were used as extractants. Liu et al. [19] reported that NaOH treatment may lead to the conversion of 6:2 FTCA to 6:2 FTUCA. Based on the above results, MeOH was used in the following experiment.

3.4. Effect of NaOH concentration on the conversion of 6:2 FTCA and 8:2 FTCA

In order to further evaluate the effect of NaOH treatment on the conversion of 6:2 FTCA and 8:2 FTCA, the conversion kinetics of FTCAs in MeOH solution with different NaOH concentrations were monitored over 24 h. The results are shown in Fig. 4. No conversion was found for 6:2 FTCA and 8:2 FTCA in control. With the time increasing, the concentrations of 6:2 FTCA decreased, while those of 6:2 FTUCA increased gradually. At the end of the experiment, the concentrations of 6:2 FTCA in 0.01 M and 0.05 M NaOH/MeOH were 43.9 ± 0.49 ng/mL and 16.4 ± 0.63 ng/mL, which are about 88% and 33% of their original levels, respectively, while the concentrations of 6:2 FTUCA in 0.01 M and 0.05 M NaOH/MeOH were 6.33 ± 0.27 ng/mL and 33.1 ± 1.21 ng/mL, respectively (Fig. 4(a)). Similar decreases of 8:2 FTCA and increases of 8:2 FTUCA were

also found (Fig. 4(b)). The experimental data were fitted with the first-order kinetics:

$$Q_1 = Q_0 e^{-k_1 t} \quad (1)$$

$$Q_2 = Q_0 (1 - e^{-k_2 t}) \quad (2)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (3)$$

where Q_1 and Q_2 are concentrations of FTCAs and FTUCAs (ng/mL), respectively, at time t (h). k_1 and k_2 are conversion rate constants (h^{-1}) for FTCAs and FTUCAs, respectively. Q_0 is the concentration of FTCAs at the beginning of the experiment, which is 50 ng/mL. $t_{1/2}$ is the half-life of FTCAs conversion.

The conversion kinetics of FTCAs and FTUCAs satisfactorily fitted by the first-order kinetic model (Eqs. (1) and (2)), with R^2 values higher than 0.905 (Fig. 4, Table S4 in the Supplementary materials).

Table 2

Limits of detection (LODs, ng/g dw) and limits of quantification (LOQs, ng/g dw) for FTOHs and poly- and perfluorinated acids in soil and plant matrices.

Analytes	Soils		Plants	
	LOD	LOQ	LOD	LOQ
6:2 FTOH	0.12	0.38	0.46	1.52
7:2 sFTOH	0.04	0.11	0.14	0.44
8:2 FTOH	0.11	0.37	0.44	1.46
PFBA	0.06	0.20	0.24	0.80
PFPeA	0.03	0.10	0.12	0.40
PFHxA	0.02	0.07	0.08	0.26
PFHpA	0.02	0.07	0.08	0.26
PFOA	0.03	0.10	0.12	0.40
PFNA	0.05	0.15	0.18	0.58
4:3 FTCA	0.02	0.07	0.08	0.26
5:3 FTCA	0.02	0.05	0.06	0.20
7:3 FTCA	0.02	0.07	0.08	0.26
6:2 FTUCA	0.01	0.03	0.04	0.13
6:2 FTCA	0.05	0.17	0.20	0.66
8:2 FTUCA	0.02	0.05	0.06	0.20
8:2 FTCA	0.06	0.18	0.22	0.70

Table 3

Concentrations of FTOHs and poly- and perfluorinated acids (ng/g dw) in biosolids-amended soils and plants.

Analytes	Soil 1	Soil 2	Plant 1			Plant 2			Internal standards	Recoveries (%)
			Root	Straw	Leaf	Root	Straw	Leaf		
6:2 FTOH	31.2 (4.1) ^a	57.4 (5.9)	1.74 (0.03)	<LOD	1.84 (0.22)	1.97 (0.07)	<LOD	6.36 (0.59)	M6:2 FTOH	88–97
7:2 sFTOH	0.14 (0.01)	0.27 (0.02)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	N.A. ^b	N.A.
8:2 FTOH	12.8 (1.7)	25.1 (1.2)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	M8:2 FTOH	85–99
PFBA	0.64 (0.05)	0.38 (0.02)	4.02 (0.39)	9.72 (1.1)	5.16 (0.02)	2.84 (0.25)	7.92 (1.02)	10.2 (0.10)	MPFBA	78–92
PFPeA	0.14 (0.01)	0.15 (0.01)	5.20 (0.51)	25.5 (2.1)	13.2 (1.0)	5.43 (0.44)	18.2 (1.1)	8.88 (0.78)	N.A.	N.A.
PFHxA	0.18 (0.01)	0.28 (0.01)	0.40 (0.01)	2.69 (0.23)	1.53 (0.19)	0.55 (0.05)	3.78 (0.21)	1.16 (0.09)	MPFHxA	75–88
PFHpA	0.48 (0.02)	1.05 (0.12)	0.29 (0.02)	0.26 (0.03)	0.71 (0.20)	0.22 (0.01)	0.33 (0.06)	0.52 (0.26)	N.A.	N.A.
PFOA	166 (13)	347 (11)	4.43 (0.39)	0.53 (0.03)	3.18 (0.12)	4.94 (0.08)	1.08 (0.13)	5.85 (0.44)	MPFOA	82–99
PFNA	0.17 (0.01)	0.26 (0.01)	0.21 (0.01)	0.46 (0.03)	0.59 (0.04)	0.68 (0.02)	0.77 (0.05)	2.10 (0.18)	MPFNA	73–87
4:3 FTCA	0.08 (0.01)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	N.A.	N.A.
5:3 FTCA	0.03 (0.01)	0.14 (0.01)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	N.A.	N.A.
7:3 FTCA	0.10 (0.01)	0.13 (0.01)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	N.A.	N.A.
6:2 FTUCA	0.07 (0.01)	0.10 (0.01)	0.31 (0.03)	0.38 (0.02)	0.14 (0.01)	0.26 (0.07)	0.12 (0.01)	0.15 (0.01)	M6:2 FTUCA	65–81
6:2 FTCA	0.13 (0.01)	0.12 (0.01)	0.57 (0.02)	0.23 (0.02)	<LOD	0.44 (0.04)	0.29 (0.02)	<LOD	M6:2 FTCA	60–77
8:2 FTUCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	M8:2 FTUCA	80–95
8:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	M8:2 FTCA	56–80

^a Standard deviation for triplicate measurements.^b N.A., not available.

The k_1 values calculated from Eq. (1) were consistent with k_2 calculated from Eq. (2), indicating the conversion from FTCAs to FTUCAs. FTCAs in 0.05 M NaOH/MeOH presented higher k_1 and lower $t_{1/2}$ values than those in 0.01 M NaOH/MeOH, suggesting that NaOH facilitate the conversion of FTCAs. 6:2 FTCA displayed faster conversion rate than that of 8:2 FTCA. The conversion of 6:2 and 8:2 FTCAs into the corresponding FTUCAs in the presence of NaOH may be the results of elimination reactions of halogenated fatty acids, such as the following reaction:

The effects of NaOH on FTCAs conversion suggest NaOH cannot be used in the extraction of FTCAs.

3.5. Limit of detection and quantification

The LODs and LOQs are presented in Table 2. The LOQs for soil were 0.11–0.38 ng/g dry weight (dw) for FTOHs and 0.03–0.20 ng/g dw for poly- and perfluorinated acids; while those for plant tissue were 0.44–1.52 ng/g dw for FTOHs, and 0.13–0.80 ng/g dw for poly- and perfluorinated acids, respectively. Yoo et al. [7,27] used EtOAc and MTBE to extract FTOHs from sludge-applied soils and plants, respectively, and directly analyzed by GC/MS without further cleaning. Their LOQs for FTOHs were 0.9–3.2 ng/g dw for soil, and 0.5–1.0 ng/g dw for plant tissues. Our LOQs for FTOHs are equivalent to theirs.

3.6. Analysis of environmental samples

FTOHs and poly- and perfluorinated acids in soil and plant samples collected from biosolids-amended agricultural fields were extracted by MeOH and cleanup by activated graphitized carbon cleanup and WAX-SPE, respectively. The samples were analyzed in triplicate to establish the accuracy of the measurements. The extraction recoveries of isotope-labeled internal standards were 85–99% for FTOHs, 73–99% for PFCAs, and 56–95% for FTCAs and FTUCAs (Table 3). No significant difference of recoveries between soils and plant tissues was found (data not shown).

6:2 FTOH and 8:2 FTOH were found in two biosolids-amended soils, with the total concentrations ranged from 12.8 to 57.4 ng/g dw. This level was comparable to that reported in biosolids-amended soils in Decatur, Alabama [27]. Only 6:2 FTOH was found in plant roots and leaves. 8:2 FTOH in plant tissues was under its limit of detection. This may suggest that 8:2 FTOH was less labile to

transfer from soil to plant when compared with 6:2 FTOH. Chemical compounds reach aerial plant organs in two ways: from the air and with the transpiration stream. The findings that 6:2 FTOH accumulations in leaves, while did not in straws indicated the foliar uptake from the air.

PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA were detected in soils and plant roots, straws and leaves. These PFCAs were considered the possible final degradation products of 6:2 FTOH and 8:2 FTOH [21]. Among these PFCAs, the one with the highest concentrations detected in soils were PFOA. However, it is worthy to note that the PFCAs in soils may be derived from the biodegradation of FTOHs and other related precursors currently in use [46], as well as direct introduction from biosolids [30]. The PFCAs in plants may be from direct plant uptake and precursor degradation within plants.

7:2 sFTOH, 7:3 FTCA, 8:2 FTCA and 8:2 FTUCA were reported to be the possible intermediate degradation products of 8:2 FTOH [18,21]. The existence of 7:2 sFTOH (0.14 and 0.27 ng/g dw) and 7:3 FTCA (0.10 and 0.13 ng/g dw) in soils gave direct evidences for the degradation of 8:2 FTOH in biosolids-amended soils under field condition. As the intermediate degradation products of 6:2 FTOH, 6:2 FTCA and 6:2 FTUCA were found in plant roots and straws. Moreover, the concentrations of 6:2 FTCA and 6:2 FTUCA in plants were higher than those in soils. This implied that not only soil microbes, but also plant may have the ability to degrade 6:2 FTOH.

4. Conclusions

In the present study, MeOH was selected to extract 6:2 FTOH, 8:2 FTOH, and their degradation products 7:2 sFTOH and 13 poly- and perfluorinated acids from soils and plants simultaneously. NaOH in extractant facilitate the conversion of 6:2 and 8:2 FTCAs into the corresponding FTUCAs, thus should be avoided. FTOHs and poly- and perfluorinated acid extracts can be cleaned up by Envi-Carb graphitized carbon and WAX-SPE, respectively, prior to quantitative determination using UPLC–MS/MS. They were found in all the biosolids-amended agricultural soil and plant samples. This finding demonstrated contamination of FTOHs in soils and plants as a result of biosolids-amendment, and the degradation of FTOHs in soil-plant system. This paper firstly reported the quantitative determination of FTOHs and their degradation products in biosolids-amended soils and plants, and the methods developed here can be used to investigate the occurrence and fate of FTOHs in terrestrial environment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chroma.2015.05.063>

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