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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.

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 ≥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. Tetrabutyl 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 μm) 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, Firlawn, 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° 20′ N, 116° 38′ 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 μL 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 × *g*, 20 min) to consolidate the EtOAc fraction. This extraction step was repeated twice. All organic