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Uptake and metabolism of 10:2 fluorotelomer alcohol in soil-earthworm (*Eisenia fetida*) and soil-wheat (*Triticum aestivum* L.) systems☆

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ABSTRACT

The behavior of 10:2 fluorotelomer alcohol (10:2 FTOH) in the systems of soil-earthworm (*Eisenia fetida*), soil-wheat (*Triticum aestivum* L.) and soil-earthworm-wheat, including degradation in soil, uptake and metabolism in wheat and earthworms were investigated. Several perfluorocarboxylic acids (PFCAs) as degradation products of 10:2 FTOH were identified in the soil, plant and earthworms. 10:2 FTOH could be biodegraded to perfluorooctanoate (PFOA), perfluorononanate (PFNA) and perfluorodecanoate (PFDA) in soil in the absence or presence of wheat/earthworms, and PFDA was the predominant metabolite. Accumulation of initial 10:2 FTOH and its metabolites were observed in the wheat and earthworms, suggesting that 10:2 FTOH could be bioaccumulated in wheat and earthworms and biotransformed to the highly stable PFCAs. Perfluoropentanoic acid (PFPeA), perfluorohexanoic (PFHxA) and PFDA were detected in wheat root, while PFDA and perfluoroundecanoic acid (PFUnDA) were detected in shoot. PFNA and PFDA were determined in earthworms and the concentration of PFDA was much higher. The presence of earthworms and/or plant stimulated the microbial degradation of 10:2 FTOH in soil. The results supplied important evidence that degradation of 10:2 FTOH was an important potential source of PFCAs in the environment and in biota.

1. Introduction

Due to the ability to repel both water and oil, per- and polyfluoroalkyl substances (PFASs) including ionic PFASs and their precursors are world-widely used as surfactants, such as in paper, refrigerating fluid, textiles, lubricant, film-forming foams, cosmetics, cleaners and food packaging (Buck et al., 2011; Paul et al., 2009). During the production or use of PFASs and their precursors, they can be released in the ambient matrices, such as surface water, soil and sediment (Higgins et al., 2007; Lindstrom et al., 2011; Paul et al., 2009; Yoo et al., 2010). Due to the strong binding potential to proteins, PFASs can be bioaccumulated in organisms and humans, biomagnified through food chains (D'eon and Mabury, 2011; Higgins et al., 2007; Jeon et al., 2010; Loi et al., 2011; Müller et al., 2011; Yoo et al., 2011) and display toxicities to humans and wildlife (Lau et al., 2007). It is therefore particularly important to investigate the fates of PFASs in the environment.

Fluorotelomer alcohols (FTOHs, $F(CF_2CF_2)_nCH_2CH_2OH$), with even-numbered fluorocarbon chains and an ethanol moiety, are a group of important PFASs. They are typically used as precursors in the production of fluorinated polymers, which are used in various commercial products such as clothing, upholstery, carpeting and fast-food packaging since telomerization became the main industrial synthetic method (Dinglasan et al., 2004; Yuan et al., 2016). FTOHs (4:2–16:2) have been found in rainwater, surface and groundwater, wastewater, soil, air and house dust, aquatic biota and plants (Houde et al., 2011; Lindstrom et al., 2011; Stock et al., 2004; Yoo et al., 2010, 2011; Zhang et al., 2015). Studies indicated that they can be degraded through abiotic (Ellis et al., 2004; Gauthier and Mabury, 2005; Wallington et al., 2006) and biological routes (Lindstrom et al., 2011; Liu et al., 2007; Yoo et al., 2010) and the usual final products are PFCAs due to breakdown of FTOHs beyond

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ethanol moiety and formation of metabolites with equal or less than parent fluorinated carbons (Wang et al., 2005a). There herein, exposure to FTOHs represents an indirect source of PFCAs and significantly contributes to the burden of PFCAs observed in environment and humans.

Soil is an important reservoir of 10:2 FTOH [$F(CF_2)_{10}CH_2CH_2OH$] as well as longer-chain FTOHs in the environment due to their strong adsorption capacities to soil/sediment (Liu and Lee, 2007). It was reported that the concentration of 10:2 FTOH in sludge-applied soils near Decatur, Alabama, USA was in the range of 0.1–166 ng/g dry weight (Yoo et al., 2010). Many previous studies indicated that PFCAs in soil could be bioaccumulated by plants (Blaine et al., 2013, 2014a, 2014b; Müller et al., 2016) and earthworms (Zhao et al., 2014), and *n*-ethyl perfluorooctane sulfonamido ethanol (N-EtFOSE), which is a precursor of perfluorooctane sulfonate (PFOS), could be accumulated from soil and biotransformed to PFOS in earthworms (*Eisenia.andrei*) (Zhao et al., 2016). Several previous studies demonstrated the biotransformation of PFCA precursors to PFCAs in rat, mice, rainbow trout and plants (Brandsma et al., 2011; Butt et al., 2010; Kudo et al., 2005; Martin et al., 2004; Nabb et al., 2007; Yoo et al., 2011; Zhang et al., 2015). Brandsma et al. (2011) reported that 10:2 FTOH could be bioaccumulated in rainbow trout (*Oncorhynchus mykiss*) and metabolized to fluorotelomer saturated (FTCAs) and unsaturated acids (FTUCAs) and perfluorodecanoate (PFDA). Yoo et al. (2011) determined FTOHs and PFCAs in plants from a biosolid-amended field soil and speculated that plants could take up FTOHs from soil or air and then biotransform them to PFCAs. Zhang et al. (2015) detected FTOHs (6:2 and 8:2) and their possible metabolites such as PFCAs, FTCAs and FTUCAs in soils and plants from biosolid-amended field. Bizkarguenaga et al. (2016) found that 8:2 perfluoroalkyl phosphate diester (8:2 diPAP) could be taken up and biotransformed to FTCA, FTUCA and PFCAs in crop from compost-amended soil. All these studies suggested that FTOHs could be accumulated and degraded to PFCAs in earthworms and plants, which implies a risk to the terrestrial ecosystem considering that the final end product PFCAs are more toxic, persistent and bioaccumulative (Mejia Avendano and Liu, 2015). However, little has been done to understand the bioaccumulation and biotransformation of FTOHs in earthworms and plants.

The objective of the present study was to investigate the accumulation and metabolism behaviors of 10:2 FTOH in soil-biota systems using greenhouse pot experiments. Four individual systems were set-up: soil, soil-earthworm, soil-wheat, and soil-earthworm-wheat, to understand the individual effects of microorganisms, earthworms and plants and their combined effects. 10:2 FTOH and possible degradation products were monitored in soil, earthworms (*Eisenia fetida*) and wheat (*Triticum aestivum* L.). The results are helpful to understand the bioaccumulation and biodegradation of 10:2 FTOH in the soil-biota systems.

2. Materials and methods

2.1. Chemicals

Perfluoropentanoic acid (PFPeA, 97%) and perfluorohexanoic (PFHxA) and 1H,1H,2H,2H-perfluoro-1-dodecanol (10:2 FTOH, 98%) were purchased from Alfa Aesar Co., Ltd (Tianjin, China). Perfluoroheptanoic acid (PFHpA, 98%), perfluorooctanoic acid (PFOA, 95%) and perfluorononanoic acid (PFNA, 97%) were purchased from Shanghai Adam Beta Reagent Co., Ltd. (China). Perfluorodecanoic acid (PFDA, 96%) and perfluorododecanoic acid (PFDoA, 97%) were obtained from Geel, Belgium (New Jersey, USA). Perfluoroundecanoic acid (PFUnDA) was purchased from FluoroChem Ltd. (United Kingdom). Methanol of high-performance liquid chromatography (HPLC) grade was purchased from Teda Chemical Company (Tianjin, China). Dichloromethane (DCM) and methanol for extraction were purchased from Concord Science and Technology. Other chemicals were bought from Weida Chemical Commercial Ltd. (Tianjin, China).

2.2. Soil properties and treatment

Surface soil (0–10 cm) was collected from a farm southwest of Tianjin, China, that is without detectable PFASs. The soil selected characteristics are as follows: pH, 7.67; organic matter content, 4.11%; cation exchange capacity (CEC), 38.47 cmol/kg; moisture content for air-dried soil, 1.03%; clay, 24%, silt, 64% and sand, 12%. The soil was air-dried for 14 days and sifted through a 2-mm sieve. The dried soil received basal fertilizers at rates of 100 mg P (KH2PO4), 300 mg N (NH4NO3) and 200 mg K (K2SO4)/kg soil. About 200 g of pre-weighed soil was spiked with one mL of the mixed solution of 10:2 FTOH dissolved in methanol and mixed thoroughly, and then placed in a fume hood for solvent evaporation for 24 h. Nonspiked soil was continuously added to the spiked soil and then mixed thoroughly until all the pre-weighed soil was mixed, which was shaken for 5 times (30 min/each time) each day for 6 d continuously. The soil was then incubated in dark for 14 d at room temperature. The concentrations of the target PFASs in the soil were measured after incubation and also at the end of the experiment. The concentration of 10:2 FTOH in the soil after incubation but before the exposure test was 0.144 nmol/g and no PFCAs were detected in the soil. This suggested that the transformation of 10:2 FTOH to PFCAs in the dry soil during the incubation period was negligible.

2.3. Exposure and sampling

Plastic pots were packed with 650 g (volume was 0.9 l) of spiked soil. Five groups of tests were conducted: 1, a control test in which the soil was clean without spiking 10:2 FTOH (namely C group); 2, soil alone, which was spiked with 10:2 FTOH but without either earthworms or wheat (S). 3 and 4, wheat (*Triticum aestivum* L.) and earthworms (*Eisenia fetida*) were cultured individually in spiked soil (W and E groups). 5, wheat and earthworms were co-cultured in spiked soil (W + E). Each group test was conducted with triplicates in three parallel pots. The soil was brought to 60–70% of water holding capacity by adding distilled water in the soil. All the pots were capped with nylon net (0.2 mm mesh) to prevent the worms from escaping during exposure.

Mature worms (*Eisenia fetida*) were obtained from an earthworm culture farm (Tianjin, China) and were cultured in the laboratory for 14 days. Distilled water was added as required to maintain moisture prior to addition of the earthworms. In the E and W + E groups, around 10–13 earthworms (approximately 4 g wet weight) were added in each pot. After 30 exposure days, the earthworms were sifted from the soil, washed with distilled water and allowed to purge for 24 h on clean filter paper. The sampled earthworms were freeze-dried, ground to homogenized samples and stored at −20 °C before chemical analysis.

Wheat seeds (*Triticum aestivum* L., purchased from the Chinese Academy of Agricultural Sciences, Beijing, China) were sterilized in 3% H_2O_2 solution, washed with distilled water, soaked in 2.8 mmol/L $Ca(NO_3)_2$ solution for 4 h in dark, and then germinated on moist filter paper at 22–27 °C. After germination for 3 days, uniform seedlings were sown in plastic pots (10 plants/pot) of group W and W + E, which were placed in plant growth chamber for 14 h at 27 °C (day) and for 10 h at 22 °C (night). Wheat was irrigated daily with distilled water to maintain soil moisture at 60–70% of water holding capacity by weight. All the pots, including the control