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Aerobic biodegradation of 8:2 fluorotelomer stearate monoester and 8:2 fluorotelomer citrate triester in forest soil

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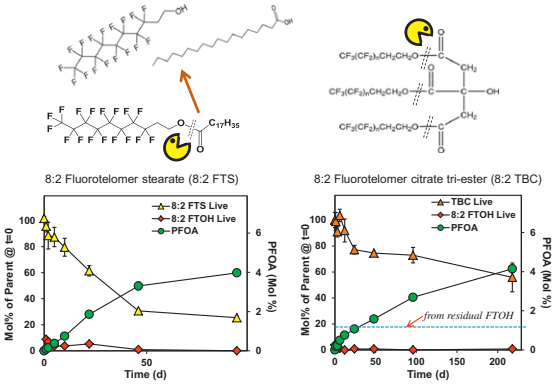
HIGHLIGHTS

- The half-life of fluorotelomer stearate, FTS, is <1 month in an aerobic soil.
- Cleavage of the ester bond was evident by release of 8:2 FTOH and stearic acid.
- Production of PFOA resulted from the biotransformation of both FTS and TBC.
- Degradation of fluorotelomer citrate tri-ester (TBC) was slow.
- Prolonged cold storage of the forest soil, increased hydrolysis rates.

GRAPHICAL ABSTRACT



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ABSTRACT

Aerobic biodegradation of 8:2 fluorotelomer stearate (FTS) and 8:2 fluorotelomer citrate triester (TBC) was evaluated in a forest soil in closed bottle microcosms. Loss of parent, production of 8:2 fluorotelomer alcohol (8:2 FTOH), which is released along with stearic acid (SA) by microbial ester linkage, and subsequent metabolites from FTOH degradation were monitored for up to 7 months. Soil microcosms were extracted with ethyl acetate followed by two heated 90/10 v/v acetonitrile/200 mM NaOH extractions. Cleavage of the ester linkage in the 8:2 FTS occurred ($t_{1/2} \sim 28$ d), producing 8:2 FTOH and various levels of subsequent metabolites. Quantifying the generation of SA from ester cleavage in FTS was complicated by the natural production and degradation of SA in soil, which was probed in an additional FTS and SA study with the same soil that had been stored at 4 °C for 12 months. In the latter study, FTS degraded faster ($t_{1/2} \sim 5$ d) such that SA production well above soil background levels was clearly observed along with rapid subsequent SA degradation. Cold storage was hypothesized to enrich fungal enzymes, which are known to be effective at hydrolytic cleavage. 8:2 TBC biotransformation was slow, but evident with the production of PFOA well above levels expected from known FTOH residuals. Slower degradation of TBC compared to FTS is likely due to steric hindrances arising from the close proximity of three 8:2 FT chains on the citrate backbone limiting the enzyme access.

1. Introduction

The presence of perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs) in various environmental matrices (Higgins et al., 2005; Sinclair and Kannan, 2006; Oono et al., 2008; Yamashita et al., 2008), humans and wildlife (Houde

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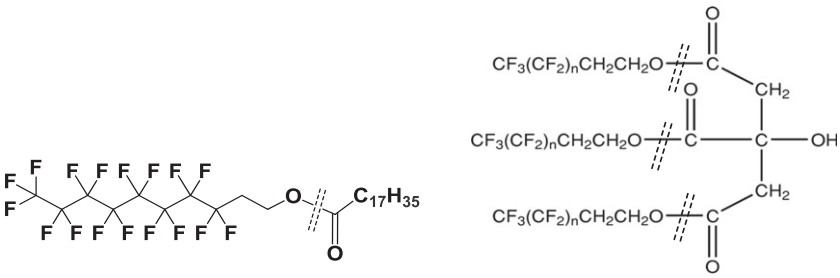

Fig. 1. Chemical structure of 8:2 fluorotelomer stearate monoester (730.6 g mol^{-1}) and 8:2 fluorotelomer citrate triester (1530.4 g mol^{-1}). The double slash indicates expected point of ester hydrolysis releasing 8:2 FTOH and stearic acid.

et al., 2006; Kato et al., 2011) and their toxicological responses to animals in laboratory studies (Lau et al., 2007) have raised concerns globally. Concerns led to combined efforts by EPA and industry to reduce direct emissions, minimize residuals in commercial products, and identify other indirect sources of these perfluoroalkyl substances (Ritter, 2010). In addition, in January 2009, the USEPA announced a Provisional Health Advisory values for perfluorooctanoic acid (PFOA) of 0.4 μg L^{-1} and perfluorooctanesulfonic acid (PFOS) of 0.2 μg L^{-1} for protecting drinking water (USEPA, 2009a).

One of the recognized indirect sources of PFOA are the fluorotelomer alcohols (FTOHs) (Wang et al., 2005a,b, 2009; Liu et al., 2007, 2010), which are used to synthesize a variety of fluorotelomer (FT) monomers by linking them to hydrocarbon backbones with ester, ether or urethane linkages (Kissa, 2001). These monomers are polymerized to specialty polymers and surfactants offering stain repellent properties used in a variety of product lines including common consumer use items such as carpets, clothing, and food wrapping (Rao and Baker, 1994; Kissa, 2001). FT polymer production was estimated around 20 million pounds in 2006 (USEPA, 2009b). FT monomers may be released during manufacturing and are present as residuals in consumer products, thus also released during consumer use and disposal activities including of wastewater treatment wastes. FT acrylate monomer was detected in some of the sludge applied soils in Decatur, AL (Yoo et al., 2010). FT monomers themselves are susceptible to degradation, and hence a potential source of PFCAs in the environment (USEPA, 2009b; Buck et al., 2011). In an aerobic biodegradation study with a loam surface soil, 8:2 fluorotelomer stearate monoester (8:2 FTS) was shown to degrade (half life <2 weeks) to 8:2 fluorotelomer alcohol (8:2 FTOH) and subsequently a suite of PFCAs including PFOA (Dasu et al., 2012).

The present work focuses on the evaluation of the biodegradation potential of 8:2 FT citrate tri-ester monomer (commercially known as Zonyl® TBC, thus referred to as 8:2 TBC here) in a forest soil relative to the 8:2 FTS monoester (Fig. 1). Both of these FT esters are used in water and oil-repellent textiles (Wu, 1994; Oharu, 2000; DuPont Technical Bulletin). Stability of these monomers was measured by quantifying the loss of parent and production of primary and secondary metabolites over time. It was hypothesized that enzyme access to the ester linkage in TBC would be more restrictive leading to its higher stability in soil compared to 8:2 FTS. Ester cleavage is anticipated to yield FTOH as observed in a previous study with 8:2 FTS in an agricultural soil (Dasu et al., 2012). For FTS, stearic acid (SA) should also be released (Fig. 1). Dasu et al. (2012) were not able to confirm SA production, which was hypothesized to be due to native SA and rapid SA biodegradation. The latter hypothesis was probed in the current study.

2. Materials

2.1. Chemicals

Purified 8:2 fluorotelomer stearate (FTS, 99.8%) and 8:2 fluorotelomer citrate (TBC), 8:2 FTOH (99%), 8:2 FT carboxylic acid (8:2 FTCA, 97%), 8:2 FT α,β-unsaturated carboxylic acid (8:2 FTUCA, 98%), 2H,2H,3H,3H-pentadecafluorodecanoic acid (7:3 FTCA, 98%), 2H,2H,3H,3H-pentadecafluorodecenoic acid (7:3 FTUCA, 98.4%), 2H-pentadecafluoro-2-nonanol (7:2 sFTOH, 80%), and the internal standards [1,1,2,2-D_4; 3-^{13}C] 8:2 FTOH (96%) and [1,2-$^{13}C_2$] PFOA (96.4%) were obtained from DuPont (Wilmington, DE). Perfluorohexanoic acid (PFHxA, 97%) and perfluorooctanoic acid (PFOA, 97%) were purchased from Oakwood Products, Inc. (West Columbia, SC) and perfluoroheptanoic acid (PFHpA, 99%) was obtained from Sigma–Aldrich (St. Louis, MO). All fluorinated chemicals were used as received and concentrations were not corrected for impurities except for 7:2 sFTOH. Stearic, palmitic and myristic acids (all ⩾99%) were purchased from Fluka. Medical grade talc powder was purchased from Fisher Scientific (Pittsburgh, PA). All other materials are detailed in Supplemental information (SI).

2.2. Soil

Biotransformation studies were conducted using a forest silt loam (FRST-44) with 5.3% organic matter and pH = 5.4 collected immediately below the vegetated zone under the tree canopy of a forested area in West Lafayette, IN in July (2010) and stored at 4 °C prior to use (details in SI). Field capacity was used as the initial soil moisture level (32%) in all experiments. The main 8:2 FTS and 8:2 TBC studies were conducted after 6 months of cold storage whereas the second and shorter follow up study with 8:2 FTS and SA was conducted after 12 months of cold storage.

3. Methods

3.1. Soil microcosm setup

Microcosms consisted of 125-mL crimped amber bottles with ~10 g soil (dry wt.) in each vessel with airtight closures (butyl rubber stoppers) to allow for headspace monitoring. For both FTS and TBC, degradation in live soils and stability in solvent controls (no soil) were monitored. For TBC, autoclave-sterilized soil was also included. A sterile soil treatment for FTS had been included in previous work and showed no abiotic degradation (Dasu et al., 2012). All incubations were conducted in the dark at 22 ± 2 °C.

Live soils were pre-incubated for 6 d at field capacity prior to monomer addition. FT monomer was added to each soil microcosm via 50 mg of chemical-coated talc powder (~50 μg FTS or TBC