PRELIMINARY STUDIES ON ^{14}C-LABELED 6:2 FLUOROTELOMER ALCOHOL BIOTRANSFORMATION IN RIVER SEDIMENT

Wang N, Buck RC, Folsom PW, Wolstenholme BW

E.I. du Pont de Nemours & Company, Inc, Wilmington, Delaware, USA

Introduction

Fluorinated chemicals have been used historically due to their unique properties[1,2]. Because of their broad and historical usage, long-chain perfluoroalkyl acids (PFAAs) such as perfluorooctanoic acid (PFOA), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), and their potential precursors have been widely detected in the global environment and biota[3]. Long-chain chemistries are being phased out in developed countries and replaced with short-chain alternative products based on perfluorobutane sulfonyl (PFBS) and 6:2 fluorotelomer alcohol [6:2 FTOH, $F(CF_2)_6CH_2CH_2OH$]. 6:2 FTOH aerobic biotransformation is rapid in soil and bacterial culture, leading to two major classes of major transformation products: polyfluorinated 5:3 acid [$F(CF_2)_5CH_2CH_2COOH$] and perfluorinated carboxylic acids[4,5] (e.g., PFPeA, PFHxA, and PFBA). River sediment is a relevant environmental compartment for FTOH- and perfluorobutyl sulfonyl-based products to enter into the environment. Currently, no information is available on potential biotransformation of FTOHs such as 6:2 FTOH in aerobic sediment environment. This study aimed at determining 6:2 FTOH biodegradation potential, identifying and quantifying transformation products, and understanding the distribution of 6:2 FTOH in a sediment-water-air test system.

Materials and methods

The test substance, [1,2-^{14}C] 6:2 FTOH [$F(CF_2)_6{}^{14}CH_2{}^{14}CH_2OH$], was custom synthesized with +99% radiochemical purity and a specific activity of 29.92 mmol/mCi. The authentic standards of potential transformation products were either synthesized by DuPont or purchased from TCI America and Synquest Laboratories. The river sediment along with river water was collected from Brandywine creek in Pennsylvania. The sediment and river water were transferred into each of the 129-mL glass serum bottles and incubated at room temperature (~ 22 °C) for ~ 7 days before initiation of the biodegradation experiment. Each sample bottle contained 20 g wet sediment and 30 mL river water. The experiment was initiated by dosing ~ 41 µg of [1,2-^{14}C] 6:2 FTOH in 50% ethanol as stock solution into the sediment of each of the sample bottles and immediately mixed and crimp-sealed with a butyl rubber stopper/aluminum cap. For sterile control, the sediment and river water were autoclaved and triple antibiotics were added to each sample bottle. For matrix control, only 50% ethanol was added to the live sediment and river water to monitor headspace O_2 content during the study to approximate the O_2 content in the live sample bottles. One C_{18} cartridge was inserted into each sample bottle to allow O_2 exchange and capture potential volatile transformation products. This "semi-static system" ensured enough O_2 in the headspace during the experimental period. At various sampling time points (e.g., days 0, 2, 7, 14, 28, 56, 90), the headspace was purged into a C_{18} cartridge to capture volatile [1,2-^{14}C] 6:2 FTOH and transformation products and eluted with 5 mL acetonitrile (ACN). The aqueous phase was extracted with ACN and the sediment was extracted multiple times with ACN (1st extraction) or ACN plus NaOH (~ 25 mM final concentration, 2nd extraction). The third extraction used concentrated HCl plus ACN to recover non-solvent extractable ^{14}C (i.e., sediment bound ^{14}C residues). The first and second sediment extracts were also treated with Envicarb™ graphitized carbon to enhance 5:3 acid recovery[4,5]. The C_{18} eluent, aqueous and sediment extracts were analyzed separately to quantify ^{14}C-labled and non-radioactive transformation products by LC/ARC and LC/MS/MS[5,6,7,8].

Results and discussion

Distribution of ^{14}C counts in sediment, aqueous phase, and headspace

When [1,2-^{14}C] 6:2 FTOH was first introduced to aqueous phase, more than 90% of ^{14}C applied at day 0 partitioned to the headspace within a week due to 6:2 FTOH low water solubility and high vapor pressure. Very little was available in sediment for biodegradation. To assess sediment biodegradability, [1,2-^{14}C] 6:2 FTOH was subsequently applied directly into the sediment. Figure 1 shows the ^{14}C distribution in sediment, aqueous

phase, and headspace over 28 days. The majority of ^{14}C remained in the sediment after 28 days. The ^{14}C in the aqueous phase decreased over time due to partitioning to the headspace and to the sediment. Partitoning to the headspace was less than 3% at day 28. The sediment ^{14}C bound residues increased steadily to about 10% at day 28. Approximately 79% of ^{14}C was recovered from all the compartments mentioned above. The remainder of ^{14}C may be lost due to mineralization of the number 1 and number 2 ^{14}C carbon atoms of 6:2 FTOH to $^{14}CO_2$, which was not trapped. The results suggest that the sediment can retain 6:2 FTOH for biodegradation..

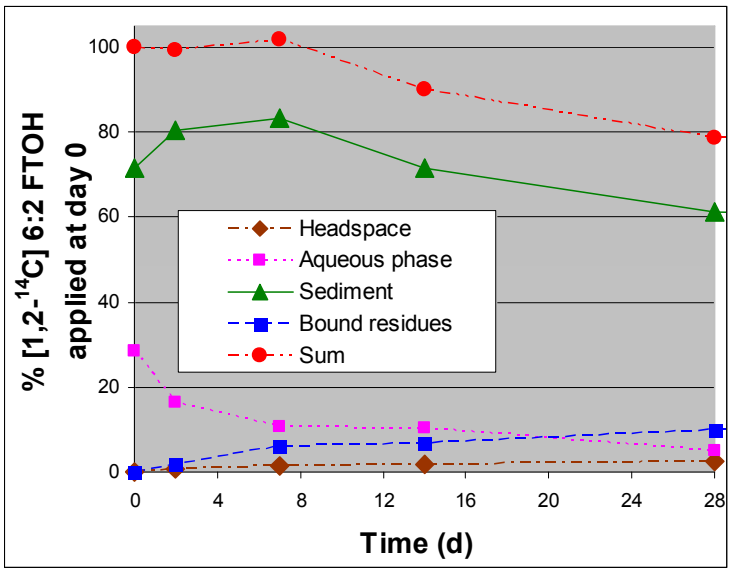

Figure 1. ^{14}C counts recovered from various compartments over 28 days.

[1,2-^{14}C] 6:2 FTOH biotransformation in aerobic sediment system

The O_2 content in the headspace of sample bottles was above 20% throughout the study period, indicating the sediment system was aerobic. [1,2-^{14}C] 6:2 FTOH was steadily converted to various intermediates and stable transformation products as shown in Figure 2. The transformation products observed are consistent with those observed in aerobic soil and enriched bacterial culture dosed with 6:2 FTOH[4]. The 5:3 acid at day 28 is the most abundant transformation product accounted for 13% of initially applied ^{14}C at day 0. The volatile intermediates 5:2 ketone [$F(CF_2)_5C(O)^{14}CH_3$] and 5:2 sFTOH [$F(CF_2)_5CH(OH)^{14}CH_3$] accounted for 5% and 7.5% at day 28, respectively. At day 28, PFHxA accounted for 4.5% and PFPeA accounted for only 0.1%, which is significantly lower than that in aerobic soil where PFPeA accounted for 30% of initially applied 6:2 FTOH[4]. No PFHpA (perfluoroheptanoic acid) was detected in samples from days 2,7,14, and 28, consistent with results observed in aerobic soil and bacterial culture[4] where PFHpA was also not detected.

The results of this study suggest that [1,2-^{14}C] 6:2 FTOH aerobic biodegradation in the sediment system described is much slower than aerobic soil yet followed similar biotransformation pathways as were observed in soil. The half-life of 6:2 FTOH in aerobic soil is less than two days[4] as compared with more than 28 days in the sediment system of this study. The results also suggest that 6:2 FTOH is not a source for PFHpA found in river sediment and also not in soil[4]. This work provides insights on 6:2 FTOH biodegradation potential in aerobic sediment system and also provides practical knowledge for environmental monitoring effort to understand the fate and distribution of poly- and perfluorinated chemicals in the environment.

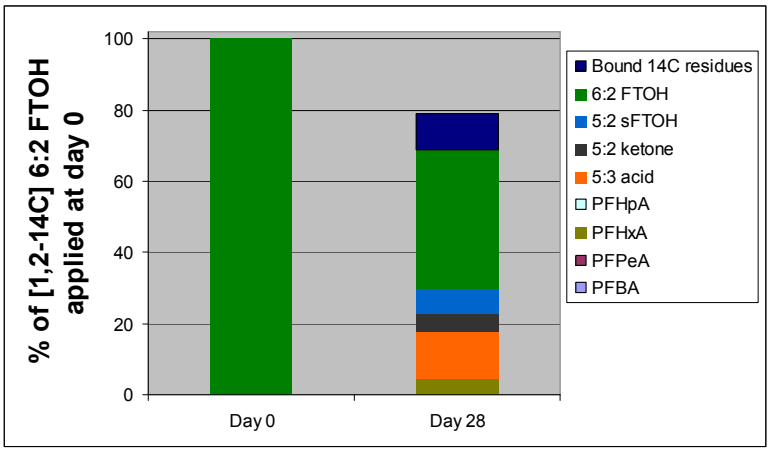

Figure 2. Mass balance and observed transformation products in aerobic sediment system. The headspace O_2 content was above 20% over 28 days. The 6:2 FTOH parent and observed transformation products are combined from sediment, aqueous phase, and headspace. The sediment bound ^{14}C residues are only from the none-solvent extractable fraction of the sediment.

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