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Determination of fluorotelomer alcohols in selected consumer products and preliminary investigation of their fate in the indoor environment

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) has established an ongoing effort to identify the major perfluorocarboxylic acid (PFCA) sources in nonoccupational indoor environments and characterize their transport and fate. This study determined the concentrations of fluorotelomer alcohols (FTOHs), which are the precursors to PFCAs, in fifty-four consumer products collected from the U.S. open market in the years of 2011 and 2013. The products included carpet, commercial carpet-care liquids, household carpet/fabric-care liquids, treated apparel, treated home textiles, treated non-woven medical garments, floor waxes, food-contact paper, membranes for apparel, and thread-sealant tapes. The FTOHs quantified were 1H,1H,2H,2H-perfluoro-1-octanol (6:2 FTOH), 1H,1H,2H,2H-perfluoro-1-decanol (8:2 FTOH), and 1H,1H,2H,2H-perfluoro-1-dodecanol (10:2 FTOH). The content of 6:2 FTOH ranged from non-delectable to 331 $\mu g\, g^{-1}$, 8:2 FTOH from non-delectable to 92 $\mu g\, g^{-1}$, and 10:2 FTOH from non-detectable to 24 $\mu g\, g^{-1}$. In addition, two consumer products from the home textile category were tested in the washing-drying process. One product from the treated apparel category and one from the home textile category were tested in the micro-scale chamber under elevated temperatures. The experimental data show that the washing-drying process with one cycle did not significantly reduce the FTOH concentrations in the tested consumer products. FTOH off-gassing was observed under accelerated aging conditions. Future tests should include air sampling to allow determination of the absolute emission rates at different temperatures. The results of this study should be informative to exposure assessment and risk management.
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1. Introduction

Perfluoroalkyl acids (PFCAs) are environmental contaminants that have prompted scientific, regulatory, and public interests because of their long-term persistence, bioaccumulation in the environment, developmental toxicity, and other health effects in laboratory animals (Taniyasu et al., 2005; Henderson and Smith, 2007; Andersen et al., 2008; Lindstrom et al., 2011; Haug et al., 2011a; Himmelstein et al., 2012). PFCAs have been detected in body fluid samples of the general population and wildlife, environmental media and consumer products (Calafat et al., 2006; Guo et al., 2009; Fiedler et al., 2010; Shoeib et al., 2011; Haug et al., 2011b; Fraser et al., 2012). Intensive research has been conducted to study their sources, fate, transport, and distribution in environmental media, human exposure, and ways to reduce the health risks. Fluorotelomer alcohols (FTOHs) are major precursors of PFCAs and other related compounds because FTOHs can ultimately degrade to form PFCAs through atmospheric oxidation (Ellis et al., 2004; Young and Mabury, 2010) and biodegradation (Nilsson et al., 2013; Butt et al., 2014). In addition, 1H,1H,2H,2H-perfluoro-1-octanol (6:2 FTOH) and 1H,1H,2H,2H-perfluoro-1-decanol (8:2 FTOH) have also been found to be estrogenic (Maras et al., 2006; Liu et al., 2010).

FTOHs are used in the synthesis of various surfactants and as intermediates in the manufacture of a variety of products with a wide range of applications including polymers, paints, adhesives, waxes, cleaning agents, etc. (Kissa, 2001; Joyce et al., 2006). FTOHs are volatile (Krusic et al., 2005) and their off-gassing from fluorotelomer-based products has been observed (Joyce et al., 2006; Sinclair et al., 2007). Schlummer et al. (2013) tested the emissions of 6:2 FTOH, 8:2 FTOH, and 1H,1H,2H,2H-perfluoro-1-dodecanol (10:2 FTOH) from selected textiles in a 10-L desiccator (25 °C and >100 air exchanges per hour) and reported emission rates up to 494 ng h^{-1}.

The estimated half-life of commercial acrylate-linked fluorotelomer polymers in soil is in the range of 10–17 years assuming degradation is surface-mediated (Washington et al., 2009). The fact

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that elevated levels of FTOHs have been widely detected in consumer products, indoor air, and house dust (Begley et al., 2005; Joyce et al., 2006; Jensen et al., 2008; Oono et al., 2008; Strynar and Lindstrom, 2008; Fiedler et al., 2010; Huber et al., 2011; Schlummer et al., 2013; Xu et al., 2013) strongly suggests the relevance of FTOH levels in the indoor environment. FTOHs have therefore contributed to the environmental distribution of PFCAs and thus to human exposure from perfluorinated compounds.

By working with eight manufacturers of perfluoropolymers and perfluorotelomers, the U.S. Environmental Protection Agency (EPA) established a PFOA (perfluorooctanoic acid) Stewardship Program in 2006 that calls for the elimination of PFOA, precursor chemicals that can break down to PFOA, and related higher homolog chemicals from emissions and products by 2015 (US EPA, 2011). In previous studies conducted by EPA, the focus was the determination of PFCAs in consumer products, including the development of methods for analyzing the contents of PFCAs in consumer articles (Liu et al., 2009), determination of the PFCA contents in samples collected from the U.S. market (Guo et al., 2009) and analysis of the market trends for PFCA contents in products (Liu et al., 2014). This paper presents the data for FTOH contents in selected consumer products. The aim of the present study was to develop analytical methods for measuring FTOHs in consumer products, determine the concentrations of FTOHs in consumer products collected from the U.S. open market and conduct a preliminary investigation into the fate of FTOHs in consumer products in the indoor environment. This information could provide insights about the sources and fate of PFCAs in the indoor environment.

2. Materials and methods

2.1. Sample collection and preparation

The consumer products were purchased from local retailers and online stores in 2011 and 2013. The samples selected for measurements were the ones with relatively high concentration of PFCAs, especially PFOA, based on the previous report (Guo et al., 2009). The ten product categories and the details of products purchased under each category are presented in Table S1. In the Table, the treated products are the ones labeled stain resistant or repellent. A total of 54 products were collected and analyzed. The product ID number consists of the category ID and a serial number. The purchased products were kept in their original package, photographed and documented with product name, vendor name, manufacturer, purchase date, price, quantity, information indicating possible use of fluorinated compounds, and other descriptive details. The products purchased in 2011 were divided into small subsamples, individually wrapped in three layers of aluminum foil, placed in a sealed plastic bag, and stored in a refrigerator at 2–4 °C. The 2011 products were shared with another project and were not analyzed for FTOHs until 2013. Products purchased in 2013 were stored in the laboratory at room temperature prior to extraction and analysis within one week of procurement.

Solid samples such as fabrics and carpets were cut from the primary sample into small coupons of more than 50 pieces, from which composite subsamples (about 0.05 g each) were randomly selected for extraction. For liquid samples, 100 μL aliquots were used for solvent extraction. Duplicate or triplicate subsample sets were prepared for each product. To investigate the variability of FTOH contents at different locations in the solid samples, six subsamples were prepared from one home textile product, a twin size mattress pad (E-2). Three evenly spaced subsamples were cut from each long side of the mattress pad. The subsample from each location was extracted and analyzed in duplicate.

2.2. Evaluation of extraction solvents

To evaluate the extraction efficiencies of different solvents, one liquid product and one solid product were extracted with methanol (HPLC grade, Fisher Scientific, Fair Lawn, NJ, USA), ethyl acetate (residue analysis grade, Honeywell Burdick & Jackson, Muskegon, MI, USA), hexane (Optima grade, Fisher Scientific) and methyl tert-butyl ether (MTBE, anhydrous, 99.8%, Sigma–Aldrich, St. Louis, MO, USA). For each product, triplicate subsamples were prepared and extracted with each solvent. The extraction followed the procedures described in Section 2.5.

2.3. Washing/drying tests

Subsamples from two mattress pads (E-1 and E-2) under the home textile category were tested to investigate if FTOHs could be released during the washing and drying processes. The washer used for the test was a Frigidaire Energy Star Gallery Series (front load, Model GLTF2940FS1, Charlotte, NC, USA) and the dryer was a Frigidaire Energy Star Heavy Duty Dryer (electrical, Model FE03323FS0). A widely used household detergent was utilized for the laundering process. The washer and dryer settings employed in the tests are shown in Table S2. The water temperature in the washer and the air temperature in the dryer were measured using calibrated thermocouple thermometers (Digi-Sense 6001-50, Cole-Parmer, Vernon Hills, IL, USA).

For each product, four groups of subsamples were prepared with each group consisting of two diamond-shaped swatches (Fig. S1). Each side of the diamond shape swatch was approximately 8 inches long. Group 1 was used for measuring the FTOH contents in the unwashed sample, Group 2 was washed and then dried in the dryer, Group 3 was washed and dried in room air, and Group 4 was not washed but placed in the dryer. Three composite subsamples were cut from the two test swatches from each group then extracted for gas chromatography/mass spectrometry (GC/MS) to determine the concentration changes of FTOHs in the samples.

2.4. Micro-scale chamber tests

A Markes micro-scale chamber/Thermal Extractor (μ-CTE) (Markes International, Inc., Cincinnati, OH, USA) was utilized to investigate the effect of temperature on the emissions of FTOH compounds from two products, a mattress pad (E-3) and membrane apparel (I-2). The μ-CTE system was operated in a fume hood (Fig. S2). The air supply was from a clean air generation system consisting of house-supplied high-pressure oil-free air, a pure air generator (Aadco model 737-11A, Cleves, OH, USA), a dryer (Hankinson model SSRD10-300, Canonsburg, PA, USA), an activated charcoal canister (Supelco, Bellefonte, PA, USA), a micro sieve canister (Supelco) and a gross particle filter (Grainger Speedaire, Chicago, IL, USA). The micro-scale chamber system contains six 44-mL Silicosteel® coated stainless steel chambers (30 mm in depth and 45 mm in diameter). The high flow-rate option was selected for the tests. According to the vendor, the air velocities across sample surfaces are roughly uniform and approximately 5 cm s^{-1} at an inlet gas flow of 350 mL min^{-1}.

Prior to a test, each chamber was cleaned with methanol, warm water, and distilled water then placed in an oven at 100 °C for 1 h. Twelve pieces of a mattress pad (E-3), 4 cm diameter, and twelve pieces of a membrane (I-2), 3 cm diameter, were cut using the selected size punch. For each of the temperature settings, two pieces of subsamples were placed in separate micro-scale chambers with spacers. The inlet air pressure was set at approximately 45 psi to achieve the desired average flow rate of 410 mL min^{-1} through each chamber. The emission tests were conducted at five