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Concentrations and trends of perfluorinated chemicals in potential indoor sources from 2007 through 2011 in the US

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HIGHLIGHTS

- The concentrations of PFCs in 35 consumer products were measured from 2007 to 2011.
- A non-parametric statistical method, the sign test, was performed.
- The PFCA contents in products have shown an overall downward trend.
- Future research is recommended.

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ABSTRACT

Certain perfluorinated chemicals (PFCs) in consumer products used indoors are potential indoor PFCs sources and have been associated with developmental toxicity and other adverse health effects in laboratory animals (Lao et al., 2007). The concentrations of selected PFCs including perfluorooctanoic acid (PFOA) and other perfluorocarboxylic acids (PFCAs), in 35 selected consumer products that are commonly used in indoors were measured from the year of 2007 through 2011. The products collected 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. They were purchased from retail outlets in the United States between March 2007 and September 2011. The perfluorocarboxylic acid (PFCA) contents in the products have shown an overall downward trend. However, PFOA (C8) could still be detected in many products that we analyzed. Reductions of PFCAs were shown in both short-chain PFCAs (sum of C4 to C7) and long-chain PFCAs (sum of C8 to C12) over the study period. There were no significant changes observed between short-chain PFCAs and long-chain PFCAs. Fourteen products were analyzed to determine the amounts of perfluoroalkyl sulfonates (PFASs) they contained. These limited data show the pronounced increase of perfluoro-butane sulfonate (PFBS), an alternative to perfluorooctanoic sulfonate (PFOS), in the samples. A longer and wider range of study will be required to confirm this observed trend.

1. Introduction

Perfluoroalkyl acids (PFAAs) came to the attention of researchers and risk managers because of their persistence, developmental toxicity and other health effects in laboratory animals (Lao et al., 2007; Lindstrom et al., 2011) and their ubiquitous presence in humans, wildlife, and environmental media (Guo et al., 2009; Haug et al., 2009, 2011; Kato et al., 2009; Butt et al., 2010; Fiedler et al., 2010; Houde et al., 2011; Shoeib et al., 2011). Investigators have reported that some consumer products may be major perfluorooctanoic acid (PFOA) sources in the indoor environment, and that indoor exposure (e.g., inhalation of dusts and dermal contact with consumer products) may constitute a significant portion of the total exposure to PFOA among the general population (Moriwaki et al., 2003; Kubwabo et al., 2005; Strynar and Lindstrom, 2008; Trudel et al., 2008). To fully understand the health and environmental risks associated with perfluorocarboxylic acids (PFCAs) and related chemicals, it is important to investigate how consumer products containing or having been treated with fluoropolymers and fluorotelomers, influence human exposure in the microenvironments of homes and offices.

A project to test the perfluorocarboxylic acid (PFCA) content of various products began in late 2006 in response to the need for data to assess the risk of human exposures to PFOA and other perfluorinated chemicals (PFCs) by EPA. PFCA contents were determined in new consumer products collected in the US market (Guo et al., 2009; Liu et al., 2009). Thirteen categories of products

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containing 131 consumer products produced in 19 countries were collected. These products were believed to have been treated with fluorinated chemicals and were analyzed to determine the amount of five to twelve carbon (C5 to C12) PFCAs they contained. 116 of the 131 samples met quality assurance acceptance criteria. It was found that the total PFCA concentrations (i.e., the sum of C5 through C12) ranged from non-detectable to 47100 ng g^{-1}, whereas the PFOA concentrations ranged from non-detectable to 6750 ng g^{-1}. Among the 13 product categories, commercial carpet-care liquids, mill-treated carpeting, treated floor waxes and sealants, and treated home textile and upholstery were potentially large PFCA sources in non-occupational indoor environments. The results provided a snapshot of the transition period during which the use of fluorotelomers and fluoropolymers in consumer products was changing rapidly. The limited data from the study suggested that the PFCA contents have been reduced in most of the tested products. The trends were uneven and many products with high PFOA content could still be found among the products.

In May 2000, 3M, the primary producer of perfluorooctane sulfonate (PFOS), announced the phase-out of its production of PFOS. However, there may still be other producers of PFOS-related compounds around the world. In 2006, eight major companies in the perfluorinated chemical (PFC) industry and the EPA jointly launched the 2010/2015 PFOA Stewardship Program. Under this voluntary program, the eight companies committed to work towards a 95% reduction of PFOA, precursor chemicals that can degrade to PFOA, and related higher homologue chemicals in manufacturing emissions and in PFCA contents in articles of commerce by 2010. The secondary goal was to work toward the elimination of these chemicals from emissions and products by 2015 (US EPA, 2011). EPA has promulgated three Significant New Use Rules (SNURs) under the Toxic Substances Control Act (TSCA) to limit any future manufacture or importation of 271 perfluoroalkyl sulfonates (PFASs) (US EPA, 2013). In addition, on August 15 2012, EPA proposed a SNUR on perfluoroalkyl sulfonates and long-chain perfluoroalkyl carboxylic (LCPFAC) chemicals used as part of carpets (US EPA, 2013). Thus, as a portion of the fluorochemical industry reformulates its products, it is anticipated that the overall content of PFOA and other PFCAs in consumer products will show a downward trend.

The project to test for PFCAs in selected consumer products was extended into a second phase to assess the market trends between 2007 and 2011. The objectives of this study were to determine how the levels of PFCAs in selected consumer products changed between 2007 and 2011 and which products were potentially major PFCA sources in indoor microenvironments. This study, requested by the EPA Office of Chemical Safety and Pollution Prevention (OCSPP), provided a means to conduct an independent assessment on the reductions of PFCA contents in consumer products, primarily driven by the PFOA Stewardship Program. Priority was given to the product categories that had the highest PFCA contents based on the prior study (Guo et al., 2009). Samples with the highest PFCA contents were selected. The results of the PFCA analyses were compared with the results acquired by Guo et al. (2009). In addition to seeking a general understanding of the time trends, this study was also intended to determine whether short-chain, fluorinated compounds are being used as alternatives and whether PFOS-related substances were still being utilized in products.

2. Materials and methods

2.1. Sample collection

Between 2007 and 2011, the selected products were purchased from local retailers and online stores for ten of the thirteen categories identified in the previous work (Guo et al., 2009). Three product categories (i.e., non-stick cookware, dental floss, and miscellaneous) were not studied due to low PFC content or low market availability. The products under ten product categories and the number and date of products purchased for each category are presented in Table 1 and Table S1 in the Supplementary material (SM). In the tables, the treated products were the ones labeled stain resistant or repellent.

A total of 95 samples from 35 products were collected and analyzed over the four-year period. Whenever possible, the exact product was purchased based on the product barcode information recorded for the original samples. This proved to be a very limiting factor for the product collection because of the ever-changing markets, especially for clothing (apparel and membranes) and carpet products. With the exception of school uniforms, exact duplicate products for apparel were impossible to purchase. The school uniforms retained the barcode identity, but some of the new products had different countries of origin. Carpets proved to be the most challenging. Carpets are manufactured in runs using the same dye and yarn formulations over the production life of a particular style. Some styles are in production for years, while others are more rapidly replaced with newer fibers and manufacturing technologies. The carpet-care solutions in both the commercial and household categories retained product continuity, as did the food contact products and non-woven medical garments. If it became necessary to replace products with similar products, the following three criteria were considered: (1) same manufacturer, (2) same product stain-resistant properties as advertised on the product label and (3) comparable formulations as presented on the product's material safety data sheet.

2.2. Sample handling, storage and preparation

After purchasing, products were kept in their original packaging and transported to the EPA laboratory, where they were photographed and the product information was logged into the sample record notebook. Upon receipt, solid products were cut into smaller subsections. Liquid products were subdivided into at least three 30-mL polypropylene vials. All archived samples were individually wrapped by three layers of aluminum foil, placed in a sealed plastic bag, and stored in an air-conditioned storage facility at 23 °C. The product ID number was given by the category ID followed by the product ID and then the purchase order number. For example, A-1-0 refers to the products in Category A, Product 1, and the first purchase. A-1-1 is the same product in Category A, Product 1, second purchase.

To investigate the variability of PFCA contents at different locations of the solid product samples, subsamples were prepared from three products: girl's uniform shirt (treated apparel), microwave cooking bags (treated food contact bag) and mattress pad (treated home textiles). The locations of the subsamples of the girl's uniform shirt were from the button collar, at each lower sleeve seam, and at the torso regions of the front and the back of the shirt (Fig. 1a), respectively. Five cooking bags from one box were sampled with 3 subsamples being cut from 3 panels of one bag (A, B, C in Fig. 1b) and one subsamples being cut at the center panel of each of the other 4 bags (B in Fig. 1b). Five subsamples were collected at the center and each edge of the top side of the mattress pad (Fig. 1c).

2.3. Sample extraction and analysis

The details of solid and liquid sample extraction and analysis process were described in Liu et al. (2012). The extracted samples were stored at 4 °C in the refrigerator in the laboratory and were analyzed within 30 d. Sample quantification was conducted using