Significant Residual Fluorinated Alcohols Present in Various Fluorinated Materials

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Polyfluorinated telomer alcohols and sulfonamides are classes of compounds recently identified as precursor molecules to the perfluorinated acids detected in the environment. Despite the detection and quantification of these volatile compounds in the atmosphere, their sources remain unknown. Both classes of compounds are used in the synthesis of various fluorosurfactants and incorporated in polymeric materials used extensively in the carpet, textile, and paper industries. This study has identified the presence of residual unbound fluoro telomer alcohols (FTOHs) in varying chain lengths (C6–C14) in several commercially available and industrially applied polymeric and surfactant materials. NMeFOSE, a perfluoroalkyl sulfonamido alcohol, was also detected in a commercially available carpet protector product. A method was developed to remove these residual compounds from polymeric and surfactant materials by dispersion in water and stripping of the volatiles using a constant flow of air and trapping on XAD resin. Using gas chromatography mass spectrometry analysis, it was determined that the fluorinated materials examined consist of 0.04–3.8% residual alcohols on a fluoro alcohol to dry mass basis. These values indicate that residual alcohols, left unreacted and unbound from the manufacturing process of fluorinated polymers and surfactants, could be a significant source of the polyfluorinated telomer alcohols and sulfonamides released into the environment. This study suggests that elimination or reduction of these residual alcohols from all marketed fluorinated polymers and fluorosurfactants is key in reducing the prevalence of perfluorinated acids formed in the environment.

Introduction

Compounding evidence has been reported recently that supports the hypothesis that fluorinated telomer alcohols (FTOHs) can act as precursors to the perfluorinated acids (PFCAs) that have been detected widely in the environment. FTOHs were found pervasive (11–165 pg m⁻²) in the North American atmosphere (1, 2) and have been identified as a source of a suite of perfluorinated acids through atmospheric degradation (3). Extensive kinetic and mechanistic studies of the FTOHs with Cl atoms and OH radicals have demonstrated the formation of PFCAs as degradation products (4, 5). It has been determined, in a number of experiments, that biotic degradation of telomer alcohols under aerobic conditions also generates these persistent environmental contaminants (6, 7). Perfluorinated acids such as PFOA have been a concern to environmental scientists and regulators in recent years due to their ubiquity in various environmental matrices, particularly in blood samples of occupationally exposed workers but most specially the general human population (8). Its carcinogenic effects (9) and developmental toxicity to rats (10) have also instigated the demand for further study of these compounds and their sources by regulators to determine potential risk, if any, to humans. It has been shown that metabolism of the 8:2 telomer alcohol in rats produces PFOA (11, 12) which has further emphasized that PFOA and other PFCAs found in human blood may be partially due to exposure to these volatile compounds (12). In addition, isomeric profiles of PFCAs detected in polar bears suggest they originated primarily from a linear isomer source (13).

Similarly, the perfluoroalkyl sulfonamido alcohols have been suggested to be precursors of perfluoroalkane sulfonates, another class of perfluorinated acids (2); they have also been detected at appreciable amounts in both outdoor (1, 2) and indoor air (14). Biotransformation studies of N-ethyl perfluoroocane sulfonamidoethanol (NEtFOSE) have confirmed the production of perfluoroocane sulfonate (PFOS) as a terminal metabolite in rats (15). PFOS like PFOA, has been detected in various environmental matrices and found resistant to degradation (16). Research in our laboratory is currently investigating whether sulfonamido alcohols undergo atmospheric degradation to produce PFOS. In response to the widespread detection of PFOS in the environment, 3M, a major manufacturer of perfluorinated sulfonamides voluntarily phased out their production of compounds with perfluoroocane chemistry in 2000–2002. These compounds include the sulfonamido alcohols, N-methyl (NMeFOSE) as well as N-ethyl (NEtFOSE) perfluoroocane sulfonamidoethanol.

The sources of both fluorotelomer and sulfonamido alcohols have yet to be clearly identified since they are not understood to be directly used in industrial or commercial applications. They are, however, largely used in the synthesis of various fluorosurfactants as well as incorporated into a wide array of fluorinated polymers.

Fluorinated polymers and surfactants have been in use for over half a century and have been incorporated into a vast array of products. These polymers are used widely in various industries such as paints, carpet, and paper coatings (17) and recently have found their way into other commercial products such as household cleaning agents (18). The widespread application of these polymers can be directly linked to their unique ability as effective surface-active agents, delivering both water and stain repellency. Fluorotelomer based polymers are characterized by a hydrocarbon backbone, from which telomer alcohols (FTOHs) of various chain lengths (C6–18, or 4:2 up to 16:2 FTOHs) are appended through ester, amide, urethane, and ether linkages (19). Polymers make up approximately 80% of the reported production in the fluorotelomer market (20). A critical question is whether the alcohols observed in the atmosphere are a consequence of the scission at the polymer linkage releasing the fluoro alcohols, or merely caused by sufficient residual material escaping directly from the fluorinated polymer or surfactants.

This investigation has specifically sought to quantify unbound FTOHs as well as the sulfonamido alcohols, hereafter referred to as “residuals”, from various fluorinated materials, prior to or following application to consumer or
industrial products to assess the potential contribution to the flux of these compounds to the environment. These residual alcohols, presumably a function of incomplete synthesis or lack of purification prior to marketing of materials (Figure 1), may be a significant source of release to the environment. Quantification and identification of residuals from seven different commercially and industrially available fluorinated materials were performed using a purge and trap method coupled with gas chromatography–mass spectrometry analysis. Commercially available materials are those that are available to retail consumers, whereas industrially applied materials are those that are not generally available to regular retail consumers but instead are recommended for the use of manufacturers and industry. All fluorinated materials studied may or may not contain other nonfluorinated components in their formulation. This study identifies a source of these precursor compounds, which may ultimately comprise a significant fraction of the contribution to the perfluorinated acids in the environment.

Materials and Methods
Chemicals and Standards. Zonyl FSO-100 and Zonyl FSE were obtained from DuPont chemicals (Wilmington, DE). Teflon Advance Carpet Protector was purchased from Kleen Kuip Supply Mart Inc. (Toronto, ON) and polyfox-L-diol was provided by Omnova Solutions Inc. (Fairlawn, OH). Motor–master windshield fluid with Teflon was purchased from Canadian Tire (Toronto, ON); Scotchgard Rug and Carpet Protector was purchased from Home Depot (Toronto, ON). Fluorotelomer alcohols (FTOHs) 4:2, 6:2, 8:2, and 10:2, and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl protomer alcohol (NMeFOSE) were purchased from Home Depot (Toronto, ON) and polyfox-L-diol was provided by Omnova Solutions Inc. (Fairlawn, OH). Motor–master windshield fluid with Teflon was purchased from Canadian Tire (Toronto, ON). Distilled deionized water (500 mg) (Supelco, Bellefonte, PA) and gas diffuser tubes (Pyrex, VWR International Ltd., Mississauga, ON). Distilled deionized water (500–750 mL) was added to the vessels along with 10–100 mg of the fluorinated materials of interest. These aqueous suspensions were manually shaken thoroughly and extra care was taken to ensure that the transfer of fluorinated materials to the vessels was done quickly to ensure minimal loss of volatiles. Materials that caused excessive foaming such as Zonyl FSO-100 and Zonyl FSE, were put on a shaker at 140 rpm for continuous mixing. The vessels were tightly sealed and carbon filtered in-house air was sparged through the vessels at a flow rate of ~40 mL min⁻¹. Vessels were stored at room temperature. A schematic of the experimental setup can be found in the Supporting Information. Each compound was analyzed, generally in triplicate or N = 6, and a blank vessel was included for each batch of experiments. Blank vessels consisted of deionized water without addition of any fluorinated material and were treated the same as the spiked vessels. Vessels were purged continuously for duration of up to 3 weeks with intermittent sampling of the XAD cartridges. The XAD resin and the glass wool from the cartridges were extracted using two 5 mL aliquots of ethyl acetate and both fractions were subsequently combined. Samples of 2 mL each were then transferred to autosampler vials for gas chromatographic analysis. Scotchgard spiked samples were blown down to a final volume of 200 µL using a gentle stream of purified nitrogen prior to analysis due to higher detection limits for NMeFOSE but were otherwise prepared analogous to the other materials studied. New cartridges were installed in the vessels after each sampling period.

Instrumental Analysis and Quantification. Sample analyses were carried out using a Hewlett-Packard 6890 gas chromatograph equipped with a 5973 inert mass spectrometer detector. Optimal separation of the FTOHs and NMeFOSE was done using a 30 m Rtx-35MS with Intra Guard column (0.25 mm i.d., 0.5 µm film thickness, Chromatographic Specialties, Brockville, ON). The following GC oven program was employed: initial temperature of 45 °C held for 2 min; 10 °C min⁻¹ ramp to 95 °C; 30 °C min⁻¹ ramp to 150 °C min⁻¹; 7 °C min⁻¹ ramp to 180 °C; and a final ramp of 50 °C min⁻¹ to 240 °C and held for 2 min. Helium was used as the carrier gas at a flow rate of 1 mL min⁻¹ with pulsed splitless injection at an initial pressure of 20 psi at 220 °C for 1.2 min followed by an injector purge at 40.0 mL min⁻¹ for 0.8 min. Definitive identification of fluoro alcohols was performed under both electron ionization (EI) and positive chemical ionization (PCI) modes. Quantification proceeded under PCI in single ion monitoring mode, and the molecular ion (M + 1) was monitored for all target analytes (4:2, 6:2, 8:2, 10:2, and NMeFOSE). Calibration was performed using external standards prepared in ethyl acetate and ranging in concentration from 25 to 500 pg µL⁻¹ for the telomer alcohols and 2.5 to 500 ng µL⁻¹ for the NMeFOSE. Standards

FIGURE 1. Stylized schematic of postulated steps leading to the production of telomer-based polymers using 8:2 FTOH as an example. The potential source of unreacted telomer alcohols is depicted from the reaction producing the monomer and leading to its point of release to the environment from polymeric materials if left unpurified. Polymeric materials produced will have a mixture of varying chain lengths of perfluorinated and hydrocarbon chains as well as varying carbon backbone depending on reactants used.

Preparation of Experimental Vessels. Purge and trap vessels were made using 1 L media bottles (Pyrex) with caps drilled to accommodate Orbo Amberlite XAD-2 cartridges (100 mg) (Supelco, Bellefonte, PA) and gas diffuser tubes (Pyrex, VWR International Ltd., Mississauga, ON). Distilled deionized water (500–750 mL) was added to the vessels along with 10–100 mg of the fluorinated materials of interest. These aqueous suspensions were manually shaken thoroughly and extra care was taken to ensure that the transfer of fluorinated materials to the vessels was done quickly to ensure minimal
were run between each sample set (i.e., 4–6 samples) and the mean response was used to plot a calibration curve. Good linearity was obtained with typical r² > 0.98 and retention times for all analytes of interest were well conserved (± 0.04 min). Limit of quantitation was defined as the lowest standard to give a signal-to-noise ratio ≥ 10, corresponding to 25 and 2.5 ng μL⁻¹ for the telomer alcohols and NMeFOSE, respectively.

**Dry Mass Determination.** To normalize the residual fluoro alcohols measured from the various fluorinated polymers and surfactants, values presented in this investigation are expressed as mass of fluoro alcohols to dry mass of material examined. Dry masses were obtained by measuring the mass of an aliquot of the polymer or surfactant before and after storage in a desiccator at room temperature for several days. It is assumed that the fluorinated polymeric or surfactant material was not volatile and was not lost during the drying process. Some of the fluorinated materials examined contained other compounds in their formulations such as ethylene glycol along with varying amounts of water. Expressing the quantity of fluoro alcohols in this fashion was deemed as the most appropriate method for direct comparison between different materials. This expression should provide a conservative estimate of the amounts of residuals measured and a value that allows comparison across materials and further studies. It is an attempt to prevent confusion in the reporting of residual amounts. It would be preferable to report percent residual FTOHs, for example based on total FTOHs on the polymer, but this requires data that to date are not generally available.

**Quality Control and Assurance.** Spike and recovery experiments were performed to validate the applicability of the purge and trap vessels. Fluorinated material was spiked into the vessels and stripped of residuals. Known amounts of telomer alcohols and NMeFOSE were then added to the same vessels, purged, trapped, and quantified. Recovery of target analytes was > 80% ± 20 for all compounds except the 4:2 FTOH where recoveries were <50%. Breakthrough portions of the XAD cartridges were analyzed separately to ensure breakthrough of analyte did not compromise the analysis. The 4:2 FTOH was readily found in these breakthrough analyses, which suggests poor recoveries were due to inefficient trapping. Values expressed were not corrected for recovery values.

**Results and Discussion**

Recent investigations into the environmental fate of FTOHs and perfluorinated sulfonamides have provided further evidence that they undergo degradation to pervasive and recalcitrant perfluorinated acids. In earlier studies, we have suggested that fluorinated polymers and fluorosurfactants, known to incorporate these volatile compounds, may be a source of these alcohols through fugitive emission of residuals or as they degrade post-application (2, 6). In this study, seven different fluorinated materials, ranging from industrially applied to direct consumer products, were all found to consist of free or unbound fluorinated alcohols. These compounds were quantified to determine their overall contribution to the accumulation of fluoro alcohols in the atmosphere and ultimately of PFACs to the environment.

The materials analyzed included two commercially available products known as Teflon Advance Carpet Protector and Scotchgard Rug and Carpet Protector. These products are marketed as a post-application treatment for carpets to confer water and soil repellency and are readily available at hardware and carpet care retail stores. These products are relevant in the study because of their similarity to industrial scale products. Fluorinated polymers and surfactants formulated over the past decade for industrial or commercial applications are not expected to differ significantly with respect to their basic chemistry or to the presence of fluorochemical residuals (21). Teflon Advance Carpet Protector is a urethane-based material containing 15% FTOH-based copolymers (22). Scotchgard Rug and Carpet protector is reported to contain a mixture of fluoroalkyl copolymers as well as other acrylic based polymers (23). Fluorotelomer based surfactants such as Zonyl FSO-100 and Zonyl FSE were also studied. These compounds are industrial scale products obtained directly from the producer and not generally available to regular retail consumers. FSO-100 is described as an ethoxylated nonionic fluorosurfactant able to impart low aqueous surface tensions at low concentrations. It has a generic formula Rf-CH₂CH₂O-(CH₂)ₓH where Rf = F(CF₂)ₓ-CF₃; x can be 0 to ~15 and y = 1 to ~7. Its recommended applications include incorporation into caulks, paints, coatings, and adhesives (24). Zonyl FSE is a water-soluble, anionic phosphate fluorosurfactant recommended for use in floor waxes and coatings. Its structure consists of (BHCH₂CH₂O)ₚ-(O)(ONH₄), where x and y = 1 or 2 and again the Rf is a perfluorinated chain containing 1–7 carbons (25). The synthesis of fluorotelomer based polymeric compounds is also known to proceed via the polymerization of telomer-based monomers (Figure 1), hence a monomer 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (8:2 methacrylate) was also investigated to compare the amounts of residuals obtained from this unpolymerized compound to those of polymeric and surfactant type materials. Polyoxo-1, diol, a fluorinated poloxetane that is not commercially available nor industrially applied, was also a subject of this study. Polyfluoroalkanes are synthesized using the polymerization of fluorinated oxetane monomers (26). This product is an example of a well-characterized polymeric material obtained directly from industry containing an ether-based polymer linkage. Finally, a windshield washer fluid available at common hardware and retail stores in Ontario, Canada called Motomaster Windshield Washer with Teflon was also examined to determine whether new products that have recently incorporated fluorinated polymers in their formulation would also be sources of volatile fluorinated alcohols.

Unbound fluorinated alcohols were detected in all seven materials analyzed in this study. Scotchgard carpet and rug protector, the only nontelomer based material analyzed, had free NMeFOSE detected using the purge and trap method. It is important to note that this product was of the initial formulation prior to the withdrawal of perfluorocarboxyl sulfonyl fluoride (POSF) based materials and other related sulfonamides in 2000–2002 by 3M and is no longer produced. The detection of NMeFOSE as residuals clearly reflects the presence of perfluorooctyl-based compounds. All other materials consisted of free FTOHs of varying chain length. Purgiing of the Teflon Advance product resulted in detection of unbound telomer alcohols with chain lengths ranging from 8 to 14 carbons (6:2 up to 12:2 FTOHs). The 8:2 fluorotelomer alcohol (8:2 FTOH) was found in greatest abundance, followed by the 10:2 then the 6:2. The 12:2 FTOH was also identified in an earlier range finding study using solid phase microextraction (SPME) headspace analysis but was below the limit of quantitation when purge and trap analysis was utilized. The lack of authentic 12:2 FTOH standard prevented spike and recovery analysis and the low levels measured by purge and trap analysis could have been due to poor recovery of this compound. A typical GCMS chromatogram is shown in Figure 2. The identities of the telomer alcohols were confirmed using both their EI and PCI spectra (inset). Analysis applying positive chemical ionization gave a strong signal for the molecular ions m/z 365, 465, and 565 for 6:2, 8:2, and 10:2, respectively, where each telomer alcohol differs by 100 molecular mass units. The characteristic fragments 327, 427, and 527 were evident and were attributed to the loss of −HF + H₂O from the M + 1 molecular ion as
previously reported (27). In materials that contained 4:2 FTOH, the molecular ion \( m/z \) 265 and characteristic fragment 227 were observed, although in materials that contained 12:2 FTOH, molecular ion \( m/z \) 665 was the only familiar fragment observed and the expected 627 was not evident. Analysis of telomer alcohols using electron impact ionization (EI) often fails to produce a strong signal for the molecular ion, typical fragments observed however for these compounds are \( m/z \) 69, 95, and 131 (28). This was evident when EI was used to verify the presence of FTOHs from the samples.

Profiles of FTOHs removed from the other fluorinated materials investigated differed, although 8:2 FTOH appears to be the predominant material identified in the Teflon Advance (Figure 3) and polyfox-1-diol, the two known telomer-based polymeric materials used in the study. This is expected since it has been reported that telomer compounds with carbon chain length equaling 10 (8 perfluorinated carbons) is the key surface-active ingredient in polymeric materials (26). Contact angle is a physical property critical in imparting repellency, where higher contact angles decrease adhesion. It was reported that the contact angle achieved by polymers with a general structure of \( F(CF_2)_n(CF_2)O_2C(C(CH_3)CH_2)n \) where the perfluorinated chain measures 8 carbons is optimal for water and soil repellency.
TABLE 1. Total Residual Polyfluorinated Telomer Alcohols and Sulfonamides Removed from Various Fluorinated Polymeric and Surfactant Materials

<table>
<thead>
<tr>
<th>fluorinated material</th>
<th>% of dry weight of initial fluorinated materialb</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyfox-L-diol</td>
<td>0.11b (0.03)</td>
</tr>
<tr>
<td>Teflon FSO 100</td>
<td>0.34b (0.20)</td>
</tr>
<tr>
<td>Zonyl FSE</td>
<td>1.03 (0.61)</td>
</tr>
<tr>
<td>Zonyl FSE</td>
<td>3.80 (1.09)</td>
</tr>
<tr>
<td>8:2 methacrylate monomer</td>
<td>0.04 (0.01)</td>
</tr>
<tr>
<td>Motomaster Windshield Washer with Teflon</td>
<td>0.36 (0.01)</td>
</tr>
<tr>
<td>Scotchgard Rug and Carpet Protector</td>
<td>0.39 (0.06)</td>
</tr>
</tbody>
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a Data are means (standard deviations). b Average percentage of 6 experimental vessels. All other materials tested were measured in triplicate.

FIGURE 4. Cumulative residual alcohols extracted versus days purged in Zonyl FSO 100, an ethoxylated nonionic fluorosurfactant. 4:2 FTOH is not adequately retained on the XAD cartridges used and mass shown is a significant underestimation.

(17). This may explain the abundant use of the 8:2 FTOH in various fluorinated polymeric materials. The monomer or the 8:2 methacrylate (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl methacrylate), tested consisted mainly of the 8:2 FTOH as expected but it also contained small amounts of the shorter chain 6:2 FTOH. The relatively low percent residual (Table 1) is presumably due to the extensive separation steps required to isolate the 8:2 methacrylate from the other chain length methacrylates likely generated in the synthesis. Zonyl FSO-100 and Zonyl FSE contained unbound 6:2 FTOH as the primary component of telomer alcohols purged; it has been reported that 6:2 FTOH is primarily incorporated into nonpolymeric, surfactant materials (20). The Motomaster Windshield Washer was shown to contain mostly the 6:2 FTOH; it may be that the surface-active component of this consumer product is surfactant based rather than polymeric.

This study demonstrated the effective removal of the volatile compounds from fluorinated polymeric and surfactant materials by air stripping. Figure 4 shows the relationship between accumulated telomer alcohols extracted versus days purged in vessels containing Zonyl FSO-100. The majority of the volatile compounds investigated were stripped in less than 2 days and no significant increase in accumulation was observed in subsequent days. For the other materials studied (results given in the Supporting Information) accumulation of residuals ceased at various times from 1 day for the 8:2 methacrylate, to 38 days for the Teflon Advance. The method of continuous purging of the material while dispersed in water takes advantage of the inherent physical properties of the fluorinated alcohols. Telomer and sulfonamido alcohols are considered to be hydrophobic compounds that are expected to preferentially partition into air due to their high vapor pressures and low water solubility (29). Hence, the technique applied in this study is expected to be superior to more traditional solvent extraction methods of purification though it may not be applicable on an industrial scale.

Total masses of fluoro alcohols purged from headspace of fluorinated polymers and surfactants studied ranged from 0.04 to 3.8% on the basis of mass per dry mass of initial material (Table 1). In this investigation, variation was observed in three of the measured materials, Zonyl FSE, Zonyl FSO 100, and Teflon Advance. This may be attributed to nonhomogeneous consistency of materials tested. Both Zonyl products were viscous aqueous dispersions that were resistant to mixing, while the Teflon advance product was milk-like in consistency. These values are in agreement with those reported by 3M of residuals in concentration of being 1–2% or less in their final products (30). A study by Boulanger et al. (31), published after the initial submission of this manuscript, reported the measurement of residual fluorinated monomers in a single electrochemical based surface protector product. The percent residuals reported are extremely low, which is not surprising since the fluoro alcohols in this product line was the N-MethyFose alcohol (30); this dominant material was apparently not analyzed in their study.

To assess the potential contribution of residuals to the overall flux of the telomer alcohols to the environment, key assumptions need to be made. First, values obtained from this study are conservative estimates since information is lacking concerning postproduction processing that the compounds may have undergone prior to handling in our lab. It is probable that additional release of the volatile compounds occurred prior to packaging and shipping of the various materials investigated in this study. On the basis of manufacturing data in 2000–2002 telomer alcohols had an estimated global production of 5–6.5 × 10⁶ kg yr⁻¹ (20). This has increased to 11–14 × 10⁶ kg yr⁻¹ (32) perhaps related to the withdrawal by 3M of their POSF based products in 2000–2002 (2).

The method applied in this study was designed to efficiently force out the residual compounds from the materials tested. Actual rates of residual release to the environment are difficult to determine due to diverse applications of these fluorinated products, yet undoubtedly the potential exists for a significant proportion of the residual fluoro alcohols to be released. Ellis et al. in their study of the atmospheric lifetime of telomer alcohols, have reported that based on crude calculations, a flux on the order of 100 000–1 000 000 kg yr⁻¹ is needed to maintain the concentrations currently observed in the atmosphere (23). The data presented in this paper suggests the residual fluoro alcohol contribution to the atmospheric load of these chemicals is significant and may be the dominant source. Evidence supporting this is the reported measurement of the highest concentrations of these fluoro alcohols in Griffin, Georgia, a known hub for the carpet manufacturing industry. An average of 148 pg m⁻³ of telomer alcohols and 403 pg m⁻³ of sulfonamido alcohols were detected at this sampling location (2) although widespread detection of these compounds was also observed throughout the North American atmosphere. This observation indicates that release of residual fluoro alcohols may occur all along the supply chain from production, through application, into actual consumer use. These suppositions need verification by additional measurements inside and outside the manufacturing plant as well as within areas containing the coated materials. Supportive of these data is the recent paper by Shoeib et al. reporting indoor air concentrations of fluorinated sulfonamidoethanol related chemicals (34).
Removal of these volatile compounds from various fluorinated materials is critical to reduce the occurrence of fluoro alcohols in the atmosphere and ultimately minimize the contributions to perfluorinated acid accumulation in the environment. The detection of the unbound alcohols from the monomer “stage” of the process, as demonstrated by the presence of residuals from the methacrylate monomer studied here, show that perhaps these residuals are simply a function of incomplete synthesis or poor purification at the monomer step of the manufacturing process. A typical synthetic reaction where fluorinated monomeric acrylates are produced using transesterification reaction of the 8:2 FTOH along with ethyl pyruvate was reported to have an overall yield of 70% (35) indicating that unreacted material may still be present if left unpurified. Elimination of unreacted alcohols at this stage in the manufacturing process will reduce the amounts present at the polymerization step, assuming that the polymerization reaction itself does not cleave the linkage between the fluorinated alcohols and the polymeric backbone.

This study indicates the potential for a significant amount of fluorinated alcohols to be released as residuals from a suite of fluorinated materials that are industrially applied and commercially available and hence contribute substantially to the atmospheric burden of FTOHs. The ability of these compounds to undergo long-range atmospheric transport provides a means to the production of PFCAIs in the environment as they degrade. This study also suggests that direct exposure of the general population to these compounds is plausible if these materials are applied in homes and are outgassing after treatment of surfaces, including carpet, textiles, or paper products. Metabolism of these volatile precursors would then lead to the perfluorinated acids detected in human blood samples worldwide. The elimination of these precursor compounds from marketed fluorinated materials would appear to significantly reduce the likely production of perfluorinated acids in the environment; in a recent presentation to the Environmental Protection Agency, a leading manufacturer of telomer based-materials has announced the removal of residuals from their products by 2006 (32). Studies are underway in our laboratory to determine whether abiotic and biotic degradation of polymeric materials and surfactants, post-application, can release additional fluoro alcohols to the environment.

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This article was published ASAP on January 25, 2006; a revision to the POSF paragraph in the Results and Discussion section appears in the version published ASAP on February 3, 2006.

Supporting Information Available
Further information regarding the experimental setup, blank samples, spike and recovery data, amounts of fluorinated alcohols measured, average dry weights of fluorinated materials, and plots of accumulated alcohols removed versus days for the other fluorinated materials investigated. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


(30) Fluorochemical Use, Distribution and Release Overview; prepared by the 3M Company for USEPA OPPT, May 26, 1999; U.S. Environmental Protection Agency public docket AR226-0550.


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