Degradation of Fluorotelomer Alcohols: A Likely Atmospheric Source of Perfluorinated Carboxylic Acids

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Abstract

Human and animal tissues collected in urban and remote locations contain persistent and bioaccumulative perfluorinated carboxylic acids (PFCAs). The source of PFCAs was previously unknown. Here we present smog chamber studies that indicate fluorotelomer alcohols (FTOHs) can degrade in the atmosphere to yield a homologous series of PFCAs. Atmospheric degradation of FTOHs is likely to contribute to the widespread dissemination of PFCAs. After their bioaccumulation potential is accounted for, the pattern of PFCAs yielded from FTOHs could account for the distinct contamination profile of PFCAs observed in arctic animals. Furthermore, polar bear liver was shown to contain predominately linear isomers (>99%) of perfluorononoic acid (PFNA), while both branched and linear isomers were observed for perfluorooctanoic acid, strongly suggesting a sole input of PFNA from “telomer”-based products. The significance of the gas-phase peroxy radical cross reactions that produce PFCAs has not been recognized previously. Such reactions are expected to occur during the atmospheric degradation of all perfluorinated materials, necessitating a reexamination of the environmental fate and impact of this important class of industrial chemicals.

Introduction

The U.S. Environmental Protection Agency (EPA) has stated its concern over the environmental effects of long-chain PFCAs such as perfluorooctanoic acid (PFOA, C$_{8}$F$_{17}$COOH) (1). PFOA is detectable in the blood of most humans and animals worldwide (2–7), which is problematic because it is only slowly eliminated in mammals (8), is potentially toxic (9–11), has no known metabolic or environmental degradation pathway, and is potentially carcinogenic (12). PFCAs with carbon chain lengths of between 9 and 13 are more bioaccumulative than PFOA (13). PFCAs with chain lengths of 9–11 are present in wildlife at higher concentrations than PFOA, while chain lengths of 12 and 13 are comparable in concentration to PFOA (3).

The source of most PFCAs observed in the environment is unclear (1). There are no known natural sources of long-chain PFCAs. Water-soluble PFC salts are used in the processing of fluoropolymers, and as such may be expected to enter local aquatic environments directly (14). However, it is difficult to explain how involatile PFC salts would be transported to remote regions because they are removed from the atmosphere via wet and dry deposition on a time scale of a few days (15). The simplest explanation for their ubiquity in biota in remote regions is that some unknown precursor is emitted to the atmosphere and ultimately degrades to yield PFCAs.

Fluorotelomer salts (FTOHs) are plausible candidates for the “unknown” PFC precursors. FTOHs have the generic formula F(CF$_{2}$)$_{n}$CH$_{2}$CH$_{2}$OH, where n is an even number, and are named according to the relative number of fluorinated hydrogens: e.g., F(CF$_{2}$)$_{6}$CH$_{2}$CH$_{2}$OH is 8:2 FTOH. FTOHs are volatile, appear to be ubiquitous in the North American atmosphere (17–135 pg m$^{-3}$ (16, 17)), have an atmospheric lifetime (20 days) sufficient for widespread hemispheric distribution (18), and have a long perfluoroalkyl moiety. The worldwide production is 5 x 10$^{6}$ kg yr$^{-1}$, with 40% produced in North America (18).

While it is known that FTOHs are metabolically transformed to PFOA in rats (19) and through microbial metabolism (20), the atmospheric degradation mechanism of FTOHs is unknown. Smog chamber experiments were performed to investigate the possibility that FTOHs may degrade to yield PFCAs in the atmosphere. Oxidation of FTOHs in the atmosphere is initiated by reaction with OH radicals (18). In the present work we employ Cl atoms to initiate the oxidation of FTOHs. It is believed that the majority (99%) of reactions of both OH radicals and Cl atoms with FTOHs proceed via hydrogen atom abstraction from the CH$_{2}$—group bearing the alcohol functionality (18, 20). Hence, Cl atoms provide a reasonable surrogate for OH radicals in a study of the products of atmospheric oxidation of FTOHs.

Experimental Section

Chemicals. All reagents were of purity 97% or greater and were used without further purification. The 4,2,6, and 8:2 telomer alcohols, 2,2,3,3,4,4,5,5,5-nonfluorooctanoic acid, 2,2,3,3,4,4,5,5,5,5,5-dodecanoic acid, perfluorooctanoic acid, heptadecafluorononanoic acid, pentadecafluorooctanoic acid, perfluorododecanoic acid, perfluorooctanoic acid, and tridecafluorooctanoic acid were purchased from Oakwood Research Chemicals (West Columbia, SC). Heptadecafluorononanoic acid, perfluorohexanoic acid, nonadecafluorodecanoic acid, perfluorodecanoic acid, perfluorooctanoic acid, and tridecafluoroheptanoic acid were purchased from Aldrich Chemical Co. (Milwaukee, WI). Trifluorooacetic acid was purchased from Caledon Laboratories Ltd. (Georgetown, ON, Canada) and nonafluoropentanoic acid from Fluka (Oakville, ON, Canada).

Intermediate Synthesis. Polyfluorinated acids and aldehydes were synthesized using literature procedures and authenticated by use of IR, NMR, and mass spectrometry. Fluorotelomer alcohols C$_{x}$F$_{2x+2}$CH$_{2}$C(O)OH (FTACs) were synthesized using the method of Lévéque et al. (22). Perfluorinated aldehydes C$_{x}$F$_{2x+2}$C(O)H (PFALs) were synthesized by the method of Miller et al. (23). Fluorotelomer aldehydes...
Structural Isomer Determination of PFCAs in Polar Bears. Liver samples from seven polar bears were obtained from subsistence hunters in the Ittoqqortoormiit/Scoresby Sound area of Greenland between 1999 and 2001. The livers were removed from the animals post mortem and stored separately in polyethylene plastic bags. Liver samples were kept at outdoor temperatures (~30 to ~5 °C) until storage in a freezer (~20 to ~10 °C). Tissue samples were shipped at ~20 °C from Greenland and stored in a freezer (~20 to ~10 °C) until analysis. Approximately 1–2 g (wt) of each liver was used for analyses. Extraction of PFCAs from samples was performed in a manner described elsewhere (3) using an ion pairing agent. The dried extracts were reconstituted in 50 mL of distilled water for derivatization with 2,4-difluoroaniline. The derivatization method employed has been reported elsewhere (28, 29). Structural isomers of PFOA and PFNA in the volatile, derivatized sample extracts were resolved by GC/MS and determined by selected ion monitoring of the molecular ion. For comparison, an authentic standard of PFOA provided by 3M Co. which had been produced by an electrochemical fluorination method was analyzed. A paper describing details of the analytical methodology and comprehensive findings of structural isomers of PFCAs in polar bears is in preparation (30).

Results and Discussion

Atmospheric Chemistry. The in situ analysis of FTOH photooxidation products by FTIR indicated the presence of small amounts (<10% yield) of one, or more, gas-phase PFCAs. Unfortunately, due to the similarity of the IR spectra of PFCAs, and their low yields in the chamber (~10%), FTIR spectroscopy was not well suited to identification or quantification of these species. Offline analysis of the trapped smog chamber products by LC/MS—MS indicated that each FTOH yielded a PFOA having an intact perfluorinated chain (e.g., 8:2 FTOH yielded PFNA). Interestingly, LC/MS—MS analysis also indicated production of a homologous series of shorter chain PFCAs. For example, Cl atom initiated oxidation of 8:2 FTOH yielded the entire suite of PFCAs ranging from trifluoroacetic acid (TFA) to PFOA (in addition to perfluorononanoic acid). In addition to PFCAs, 19F NMR analysis indicated the presence of perfluorinated acid fluorides (i.e., RCFOFs; Figure 1). Acid fluorides will be hydrolyzed by electro spray conditions typical of LC/MS—MS to give the corresponding carboxylic acids; thus, it remains ambiguous whether the homologous series of perfluorinated acids (e.g., TFA through PFPAO) are in fact formed from the hydrolysis of acid fluorides. This discussion, however, is purely semantic because in the troposphere, the sole atmospheric fate of acid fluorides is hydrolysis to the corresponding PFCAs. For this reason, further discussion will simply refer to PFCAs.

As indicated in Table 1, a wide variety of products were identified following the Cl atom oxidation of the 4:2, 6:2, and 8:2 FTOHs. When techniques as sensitive as GC/MS and LC/MS—MS are used, it is important to consider possible artifacts caused by contamination of the samples. There are two reasons for believing that the results given in Table 1 reflect the true oxidation products of the FTOH rather than problems associated with contamination. First, samples of FTOH/Cl2/air mixtures taken prior to UV irradiation did not reveal any evidence of the products listed in Table 1. Second, as seen from Table 1, in experiments using 4:2 FTOH no products with carbon length greater than C8 were observed and in experiments using 6:2 FTOH no products with carbon length greater than C8 were observed. The chamber was exposed to 8:2 FTOH and 6:2 FTOH prior to experiments involving 6:2 FTOH. The absence of longer chain products from experiments using shorter chain precursors indicates the absence of cross contamination.

The overall yield of PFCAs from 8:2 FTOH, at an intermediate time point in the degradation, was ~5%, while
the yield of individual PFCA homologues was proportional to the chain length. For example, both PFNA and PFOA were produced at carbon yields of 1.5%, while the yield of each shorter PFCA was less than 0.5%. The overall yield of PFCAs is expected to be greater than 5% because many intermediates were still observed in these samples, a portion of which would then yield additional PFCAs upon further oxidation. Within experimental uncertainties, we were able to account for 100% of the reacted FTOH in terms of the listed products for the 8:2 FTOH experiments (see Table 1).

The data in Table 1 show that the chlorine atom initiated oxidation of FTOHs leads to the formation of small, but significant, yields of PFCAs. This raises the following question: What is the mechanism by which PFCAs are formed in the chamber, and to what degree does the oxidation of FTOHs in the smog chamber simulate that in the atmosphere? The proposed mechanism given in Figure 1 is the simplest explanation for their production. As noted in the Introduction, the products observed following Cl atom initiated oxidation of FTOHs in the smog chamber should be the same as those formed following OH radical initiated oxidation of FTOHs in the atmosphere. Hence, the mechanism shown in Figure 1 deduced from the results of Cl atom initiated experiments should provide an accurate picture of the atmospheric degradation mechanism of FTOHs in low NOx environments.

The initial step involves the reaction of OH with FTOHs to give CxF2n+1CH2CHO in 100% yield (18), whose sole atmospheric fate is reaction with O2 to give the corresponding FTAL CxF2n+1CH2COOH.

The FTAL then reacts with OH to give acyl radicals which subsequently add O2 to give an acyl peroxy radical, CxF2n+1CH2C(OOO)O. In the atmosphere, this will then react with NO, NO2, HO2, or other peroxy radicals. In the present experiments (conducted in the absence of NOx) the fate of CxF2n+1CH2C(OOO)O will be reaction with HO2 or other peroxy radicals. By analogy with the observed behavior of CH3-C(OOO)O (30) and C2F5-C(OOO)O (32), reaction with HO2 will yield the acid CxF2n+1CH2C(O)OH in approximately 25% yield. This reaction with other peroxy radicals to give an alkoxy radical, and finally react with O2 to yield the perfluorinated aldehyde CxF2n+1CHO. As shown in Figure 1, the perfluorinated aldehyde is expected to undergo analogous reactions to the FTAL, leading to formation of the perfluorinated acid CxF2n+1C(O)OH or the perfluorinated alkoxy radical CxF2n+1-O. The atmospheric fate of CxF2n+1-O is by reaction with O2 to give the perfluorinated peroxy radical CxF2n+1OO-.

The FTAL can also eliminate COF2 and, in the presence of O2, form CxF2n+1OO- peroxo radicals. While the dominant fate of CxF2n+1OO- is expected to be reaction with other peroxy radicals to form alkoxy radicals, one channel of the reaction with α-H-containing peroxy radicals will lead to formation of perfluorinated alcohols (Figure 2, eqs a and b) (33, 34).
TABLE 1. Products Observed in the Cl Atom Oxidation of FTOHs in Air

<table>
<thead>
<tr>
<th>Product</th>
<th>4:2 FTOH</th>
<th>6:2 FTOH</th>
<th>8:2 FTOH</th>
<th>8:2 FTOH (%)</th>
</tr>
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<tbody>
<tr>
<td>Perfluorinated Acids</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFNA</td>
<td>√</td>
<td></td>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td>PFOA</td>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>perfluoroheptanoic acid</td>
<td>√</td>
<td></td>
<td></td>
<td>0.32</td>
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<tr>
<td>perfluorohexanoic acid</td>
<td></td>
<td></td>
<td></td>
<td>0.24</td>
</tr>
<tr>
<td>perfluoropentanoic acid</td>
<td>√</td>
<td></td>
<td></td>
<td>0.10</td>
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<tr>
<td>perfluorobutanoic acid</td>
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<td>perfluoropropionic acid</td>
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<td>0.01</td>
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<td>trifluoroacetic acid</td>
<td></td>
<td></td>
<td></td>
<td>&lt;0.1</td>
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<tr>
<td>Fluorotelomer Acids</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>8:2 FTCA (C₉F₁₇CH₂COOH)</td>
<td></td>
<td></td>
<td>√</td>
<td>26</td>
</tr>
<tr>
<td>6:2 FTCA (C₇F₁₅CH₂COOH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4:2 FTCA (C₅F₁₁CH₂COOH)</td>
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<td></td>
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<tr>
<td>Telomer Aldehydes</td>
<td></td>
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</tr>
<tr>
<td>8:2 FTAL (C₉F₁₇CH₂CHO)</td>
<td></td>
<td></td>
<td>√</td>
<td>6</td>
</tr>
<tr>
<td>6:2 FTAL (C₇F₁₅CH₂CHO)</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>4:2 FTAL (C₅F₁₁CH₂CHO)</td>
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<td></td>
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<tr>
<td>Perfluoroaldehydes</td>
<td></td>
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<tr>
<td>C₆ PFAL (C₆F₁₃CHO)</td>
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<tr>
<td>C₈ PFAL (C₈F₁₇CHO)</td>
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<tr>
<td>C₁₀ PFAL (C₁₀F₂₁CHO)</td>
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<td>Odd Telomer Alcohols</td>
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<td>8:1 FTOH</td>
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<td>3.9</td>
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<tr>
<td>6:1 FTOH</td>
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<td>4:1 FTOH</td>
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<tr>
<td>Unreacted FTOH</td>
<td></td>
<td></td>
<td></td>
<td>8:2</td>
</tr>
<tr>
<td>Single Carbon Products</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₃OH</td>
<td>√</td>
<td></td>
<td></td>
<td>22</td>
</tr>
<tr>
<td>COF₂</td>
<td></td>
<td></td>
<td></td>
<td>2.6</td>
</tr>
<tr>
<td>CF₂O</td>
<td></td>
<td></td>
<td></td>
<td>-21</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td></td>
<td></td>
<td>91–112</td>
</tr>
</tbody>
</table>

*In the absence of NO. "v" indicates the analyte was detected in the corresponding experiment. Identification based on FTIR spectra relative to those of authentic standards. CO₂ may be formed from unwanted reactions on chamber walls; the observed yield is the upper limit. Quantification determined by the proportional TIC response in GC/EI MS. For further spectroscopic evidence concerning the 4:2 FTOH please see Hurley et al. (27). The possibility that observed products were artifacts caused by sample contamination was considered. However, samples of FTOH/Cl₂/air mixtures taken prior to UV irradiation did not reveal any evidence of the products listed in the table.

The fate of C₂⁺F₂⁻OH will be heterogeneous elimination of HF to give the acyl fluoride C₂⁺F₂⁻=C(O)F (32), which will hydrolyze in the atmosphere to give the PFCA C₃F₇=CH₂=COOH. The formation of the odd-chain-length fluorotelomer alcohols 8:1 FTOH, 6:1 FTOH, and 4:1 FTOH (Table 1) is explained by self-reaction of C₂F₅C(O)OH and C₂F₅C(O)OH, which will proceed via both radical and molecular channels, with the odd fluorotelomer alcohol being formed in the molecular channel (Figure 2, eqs c and d).

Environmental Implications of Atmospheric Chemistry.

It is reasonable to assume that reactions similar to those given in Figure 1 will occur in the atmosphere and, hence, that emission and atmospheric degradation of FTOHs will result in the global dissemination of PFASs. It should be noted that the present experiments were performed in the absence of NO₂, while in the real atmosphere NO₂ is present (particularly in polluted urban air). The proposed mechanisms by which PFASs are formed (Figure 1) involve reaction of peroxy radicals with either HO₂ or other peroxy radicals. In the presence of excess NO₂ the fate of peroxy radicals will be reaction with either NO or NO₂. The reaction of C₂F₅C(O)OH radicals with NO proceeds via an "unzipping cycle" to produce COF₂, and does not lead directly to PFCA formation (34). Reaction of C₂F₅C(O)OH radicals with NO₂ produces the thermally unstable peroxynitrate C₂F₅C(O)O₂NO₂, which will decompose back to reactants or possibly hydrolyze to give C₂F₅C(O)OH and HNO₂ (34). Competition with NO for the available peroxy radicals will decrease the overall PFCA yield, while competition with NO₂ may decrease the PFCA yield depending on the fate of the peroxyxynitrate. Given the abundance of NO, it is unlikely that the chemistry outlined in Figure 1 will play a role in typical urban air masses. However, in remote areas (e.g., Arctic environments and over the oceans) the concentrations of HO₂ and other peroxy radicals are comparable to those of NO and NO₂ (35). Given the broad similarity in rate constants for reaction of acyl peroxy and peroxy radicals with NO, NO₂, HO₂, and other peroxy radicals (31), it is likely that reactions such as those outlined in Figure 1 will play an important role in the atmospheric oxidation of FTOHs in remote locations.

In the above discussion we make the implicit assumption that atmospheric loss of PFALs is dominated by reaction with OH radicals (see Figure 1). However, at least two other loss mechanisms need to be considered, photolysis and reaction with water.

It is well established that PFALs absorb strongly in the region 300–350 nm where there is significant solar flux (36–39). Unfortunately, there are no photodissociation quantum yield data available, and it is not possible at this time to assess the importance of photolysis as an atmospheric loss mechanism for PFALs. By analogy to the case for CH₃CHO, it is expected that photolysis of PFALs will proceed via C–C bond scission, giving perfluorinated alkyl and HCO radicals as products. Photolysis will preclude formation of PFASs via the acyl peroxy + HO₂ reaction route, but will contribute to PFCA formation via the C₂F₅O₂ + HO₂ route (see Figure 1). Further research is needed to establish the rate and products of atmospheric photolysis of PFALs.

PFASs are supplied commercially as hydrates (C₂F₅O₂+CH(OH)₃). In view of the stability of the hydrates it seems reasonable to speculate that reaction with water to form hydrates may be a significant atmospheric fate of PFASs. Very little is known about the formation or fate of such hydrates, and it is not possible at this time to assess their environmental significance. It can be argued that the formation of hydrates will preclude formation of PFASs via either the acyl peroxy + HO₂ or the C₂F₅O₂ + HO₂ route and hence reduce PFCA formation from FTOH degradation. Alternatively, it can be argued that formation of hydrates opens up an efficient route to PFCA formation (reaction with OH radicals and subsequent reaction of the diol radical with O₂) that will increase PFCA formation from FTOH degradation.

Further research is needed to clarify the importance of hydrate formation in the atmospheric chemistry of PFALs.

Long-range transport and degradation of FTOHs could explain the presence of long-chain PFASs in arctic animals, and may also explain the reported contamination profile. Martin et al. (3) observed consistent PFCA concentration profiles in polar bears and other arctic animals whereby, in general, there was a decreasing trend in PFCA concentrations with increasing chain length. This trend can be explained by the fact that the atmospheric concentration of FTOHs decreases with increasing chain length (16) and explains the same overall decreasing trend of liver PFCA concentrations with increasing chain length. Despite the overall decreasing trend with perfluoroalkyl chain length, Martin et al. observed that odd-chain length PFASs exceeded the concentration of the shorter even-chain-length PFASs in the wildlife samples. We hypothesize that FTOH degradation and subsequent bioaccumulation can explain this observation. Using the degradation of 8:2 FTOH as an example, PFPA and PFNA are produced in equal carbon yields, but given that PFNA is more bioaccumulative than PFPA (13), animals that are exposed...
to these two degradation products in the environment will carry a higher load of PFNA than PFOA, with the assumption that the only source of PFOA and PFNA would be from the atmospheric degradation of the 8:2 FTOH.

Polyfluorinated materials are commercially produced by two major methods, telomerization (the process used to produce FTOHs) and electrochemical fluorination (14). Telomerization leads predominately to straight polyfluorinated chains, while electrochemical fluorination produces both linear and branched isomers. The livers of seven polar bears were extracted and analyzed for their PFCA content (Figure 3). Linear and branched PFOA was found to be present, with the ratio of linear to branched isomers being 23:1. An authentic standard of electrochemical PFOA had a ratio of 5:1, suggesting PFOA input from both sources. PFNA analysis revealed no branched isomers. The hypothesis that PFNA present in arctic animals is attributable to FTOHs (3) is strongly supported by the absence of branched isomers for PFNA; furthermore, the odd-chain-length/even-chain-length profile observed by Martin et al. (3) was clearly visible.

Thus, atmospheric degradation of FTOHs offers a qualitative explanation for the observed contamination of arctic animals with PFOA and PFNA, which, for example, were detected in polar bears between 10 and 110 ng g⁻¹ (liver wet mass), respectively. From the data in Table 1, it seems reasonable to estimate a carbon PFCA yield from the atmospheric oxidation of FTOHs in the range 1–10%. Using the estimated flux of FTOHs into the Northern Hemisphere
(100–1000 t yr⁻¹) (18), it follows that the atmospheric oxidation of FTOHs gives rise to PFCAs in the range 1–1000 t yr⁻¹. Assuming an even distribution across the Northern Hemisphere, this equates to the delivery of approximately 0.1–10 t yr⁻¹ to the Arctic, which is comparable to the annual Arctic loading of persistent organochlorine pesticides, including hexachlorobenzene (1.8 t yr⁻¹) (40). Although bioaccumulation factors, spatial variation, and accumulated burdens are also important, it is notable that hexachlorobenzene is detectable in polar bears at a concentration similar to that of PFCAs (183 ng g⁻¹) (mean wet mass of adipose) (3).

FTOH degradation is likely an important source of PFCA pollution in remote areas. The importance of the peroxy radical cross reactions, postulated to explain the formation of PFCAs, has not been recognized previously. Such cross reactions are expected to occur to some degree during the atmospheric degradation of all polyfluorinated materials, necessitating a reexamination of the environmental impact of this class of important industrial chemicals.

Acknowledgments

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Note Added in Proof

Sellevåg et al. (41) have reported an upper limit of 0.02 for the photodissociation yield of CF₂CHO suggesting, but not proving, that photolysis of longchain PFAFs does not preclude formation of PFCAs via the acyl peroxy + HO₂ reaction route.

Literature Cited