

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

DAVID A. ELLIS,[†]
 JONATHAN W. MARTIN,[†]
 AMILA O. DE SILVA,[†]
 SCOTT A. MABURY,^{*,†}
 MICHAEL D. HURLEY,[‡]
 MAD S. P. SULBAEK ANDERSEN,^{‡,§} AND
 TIMOTHY J. WALLINGTON[‡]

Department of Chemistry, University of Toronto,
 80 St. George Street, Toronto, Ontario, Canada M5S 3H6,
 Ford Motor Company, SRL 3083, P.O. Box 2053,
 Dearborn, Michigan, 48121-2053, and
 Department of Chemistry, University of Copenhagen,
 Universitetsparken 5, DK-2100 Copenhagen, Denmark

Human and animal tissues collected in urban and remote global 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 perfluorononanoic 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 polyfluorinated 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, C₇F₁₅COOH) (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 PFCA 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 PFCA 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 alcohols (FTOHs) are plausible candidates for the "unknown" PFCA precursors. FTOHs have the generic formula F(CF₂)_nCH₂CH₂OH, where *n* is an even number, and are named according to the relative number of fluorinated to hydrogenated carbons: e.g., F(CF₂)₈CH₂CH₂OH 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 × 10⁶ 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 (>90%) of reactions of both OH radicals and Cl atoms with FTOHs proceed via hydrogen atom abstraction from the -CH₂- 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, 6:2, and 8:2 telomer alcohols, 2,2,3,3,4,4,5,5,5-nonafluoro-1-pentanol, 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-heptanol, and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro-1-nonanol and perfluorohexanoic acid were purchased from Oakwood Research Chemicals (West Columbia, SC). Heptadecafluorononanoic acid, heptafluorobutyric acid, nonadecafluorodecanoic acid, pentadecafluorooctanoic acid, perfluorododecanoic acid, pentafluoropropionic acid, and tridecafluoroheptanoic acid were purchased from Aldrich Chemical Co. (Milwaukee, WI). Trifluoroacetic 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 acids C_xF_{2x+1}CH₂C(O)OH (FTACs) were synthesized using the method of Lévêque et al. (22). Perfluorinated aldehydes C_xF_{2x+1}C(O)H (PFALs) were synthesized by the method of Miller et al. (23). Fluorotelomer aldehydes

* Corresponding author phone: (416) 978-1780; fax: (416) 978-3596; e-mail: smabury@chem.utoronto.ca.

[†] University of Toronto.

[‡] Ford Motor Co.

[§] University of Copenhagen.

$C_xF_{2x+1}CH_2C(O)H$ (FTALs) were synthesized by the method of Achilefu et al. (24).

General Smog Chamber Methods. Experiments were performed in 750 Torr of air at 296 K in a 140-L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer described in detail elsewhere (25). The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) described elsewhere (26). The oxidation of 4:2 FTOH, 6:2 FTOH, or 8:2 FTOH was initiated by reaction with Cl atoms generated by photolysis of molecular chlorine. Atmospheric oxidation of FTOHs is initiated by reaction with OH radicals. In the present work, chlorine atom initiation was used because Cl atoms are easier to generate and they react with FTOHs in the same manner as OH radicals. Initial reaction mixtures consisted of 5–7 mTorr of 4:2 FTOH, 6:2 FTOH, or 8:2 FTOH and 80–160 mTorr of Cl_2 in 750 Torr of dry (<1% relative humidity) air diluent at 296 K. Reaction mixtures were subjected to 0.5–15 min of UV irradiation, leading to consumption of FTOH in the range from 66% to >98%. FTOH loss was monitored using IR spectroscopy (18). The formation of COF_2 and CF_3OH products was monitored via IR absorption spectroscopy. The formation of other carbon-containing products was monitored as described below. Photolysis of intermediate products was not observed under these conditions and is reported elsewhere (27).

Intermediate Collection. Smog chamber samples were collected in duplicate at several time points through stainless steel tubes using precalibrated portable pumps that sampled 5 L of air at a rate of 1 L min^{-1} through 200-mg Amberlite XAD-2 cartridges (Supelco, Bellefonte, PA). XAD cartridges were eluted with methanol or ethyl acetate and analyzed by gas chromatography/mass spectrometry (GC/MS), liquid chromatography/tandem mass spectrometry (LC/MS–MS), and ^{19}F NMR. A second plug of XAD-2 resin downstream of the sample media was analyzed separately in the same manner. No analytes were observed from this sample, which suggested that trapping on the XAD-2 resin was quantitative.

Intermediate Analysis by ^{19}F NMR. NMR was performed on ethyl acetate extracts, following addition of 300 μL of deuterated acetone. All spectra were obtained at 25 °C on a Varian Unity 500 three-channel spectrometer, operating at 470.297 MHz, equipped with a 5-mm Nalorac ^{19}F proton decoupling probe. An OPH (0, 0°; 1, 90°; 2, 180°; 3, 270°) pulse phase was performed. Free induction decays (FIDs) were zero filled. Chemical shifts were recorded relative to the peak for $CFCl_3$ (0.000 ppm).

Intermediate Analysis by GC/MS. Analysis of target analytes was performed by GC/MS (Hewlett-Packard 5973 mass-selective detector) using chemical ionization in positive (PCI) and negative (NCI) modes with methane as the reagent gas (PCI, 1 mL min^{-1} ; NCI, 2 mL min^{-1}). Gas chromatographic separation was performed on a 30m DB-Wax column (0.25 mm i.d., 250-m film thickness, J&W Scientific, Folsom, CA) using helium as the carrier gas. Pulsed splitless injections (1 L) were performed at an initial pressure of 40 psi and 200 °C, returning to 10 psi at 1 min, and followed by an injector purge. The initial oven temperature was 60 °C for 1 min, ramped at 3 °C min^{-1} to 75 °C, and subsequently at 20 °C min^{-1} to 240 °C, followed by a 1-min hold. All mass spectral data were acquired in full scan mode.

Intermediate Analysis by LC/MS–MS. Liquid chromatography was performed on a Genesis C8 column using an isocratic elution program, consisting of 70% methanol/30% water (0.005 M ammonium acetate). Mass spectral data were obtained in full scan and multiple reaction monitoring (MRM) modes using a triple-quadrupole mass spectrometer equipped with an electrospray source operating in negative mode (Micro Quattro, Micromass, Manchester, U.K.).

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 (wet) 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 PFCA. 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 PFCA 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, ^{19}F NMR analysis indicated the presence of perfluorinated acid fluorides (i.e., RCFOs; Figure 1). Acid fluorides will be hydrolyzed by electrospray 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 PFOA) 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 PFCA. 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/ Cl_2 /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 C_6 were observed and in experiments using 6:2 FTOH no products with carbon length greater than C_8 were observed. The chamber was exposed to 8:2 FTOH and 6:2 FTOH prior to experiments involving 4:2 FTOH, and to 8:2 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

TABLE 1. Products Observed in the Cl Atom Oxidation of FTOHs in Air^a

product ^f	4:2 FTOH ^e	6:2 FTOH	8:2 FTOH	C mass balance, 8:2 FTOH (%)
Perfluorinated Acids				
PFNA			✓	1.6
PFOA			✓	1.5
perfluoroheptanoic acid		✓	✓	0.32
perfluorohexanoic acid		✓	✓	0.24
perfluoropentanoic acid	✓	✓	✓	0.10
perfluorobutanoic acid	✓	✓	✓	<0.1
perfluoropropionic acid	✓	✓	✓	<0.1
trifluoroacetic acid	✓	✓	✓	<0.1
Fluorotelomer Acids				
8:2 FTCA (C ₈ F ₁₇ CH ₂ COOH)			✓	26
6:2 FTCA (C ₆ F ₁₃ CH ₂ COOH)		✓		
4:2 FTCA (C ₄ F ₉ CH ₂ COOH)	✓			
Telomer Aldehydes				
8:2 FTAL (C ₈ F ₁₇ CH ₂ CHO)			✓	6
6:2 FTAL (C ₆ F ₁₃ CH ₂ CHO)		✓		
4:2 FTAL (C ₄ F ₉ CH ₂ CHO)	✓			
Perfluoroaldehydes				
C ₈ PFAL (C ₈ F ₁₇ CHO)			✓ ^b	21 ^d
C ₆ PFAL (C ₆ F ₁₃ CHO)		✓ ^b		
C ₄ PFAL (C ₄ F ₉ CHO)	✓ ^b			
Odd Telomer Alcohols^e				
8:1 FTOH			✓	3.9
6:1 FTOH		✓		
4:1 FTOH	✓			
Unreacted FTOH				
8:2			✓	6
Single Carbon Products				
COF ₂	✓	✓	✓	22
CF ₃ OH	✓	✓	✓	2.6
CO ₂	✓	✓	✓	<21 ^c
			total	91–112

^a In the absence of NO. "✓" indicates the analyte was detected in the corresponding experiment. ^b Identification based on FTIR spectra relative to those of authentic standards. ^c CO₂ may be formed from unwanted reactions on chamber walls; the observed yield is the upper limit. ^d Quantification determined by the proportional TIC response in GC/EI/MS. ^e For further spectroscopic evidence concerning the 4:2 FTOH please see Hurley et al. (27). ^f 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 C_{x-1}F_{2x-1}OH will be heterogeneous elimination of HF to give the acyl fluoride C_{x-2}F_{2x-3}C(O)F (32), which will hydrolyze in the atmosphere to give the PFCA C_{x-2}F_{2x-3}C(O)OH. 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 C_xF_{2x+1}CH₂OO[•], 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 PFCAs. It should be noted that the present experiments were performed in the absence of NO_x, while in the real atmosphere NO_x is present (particularly in polluted urban air). The proposed mechanisms by which PFCAs are formed (Figure 1) involve reaction of peroxy radicals with either HO₂ or other peroxy radicals. In the presence of excess NO_x the fate of peroxy radicals will be reaction with either NO or NO₂. The reaction of C₂F₅C(O)O₂ radicals with NO proceeds via an "unzipping cycle" to produce COF₂, and does not lead directly to PFCA formation

(34). Reaction of C₂F₅C(O)O₂ radicals with NO₂ produces the thermally unstable peroxyxynitrate C₂F₅C(O)O₂NO₂, which will decompose back to reactants or possibly hydrolyze to give C₂F₅C(O)OH and HNO₃ (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 peroxyxynitrates. 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 CH₃-CHO, 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 PFCAs via the acyl peroxy + HO₂ reaction route, but will contribute to PFCA formation via the C_xF_{2x+1}O₂ + RO₂ route (see Figure 1). Further research is needed to establish the rate and products of atmospheric photolysis of PFALs.

PFALs are supplied commercially as hydrates (C_xF_{2x+1}CH(OH)₂). 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 PFALs. 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 PFCAs via either the acyl peroxy + HO₂ or the C_xF_{2x+1}O₂ + RO₂ 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 PFCAs 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 PFCAs exceeded the concentration of the shorter even-chain-length PFCAs 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, PFOA and PFNA are produced in equal carbon yields, but given that PFNA is more bioaccumulative than PFOA (13), animals that are exposed

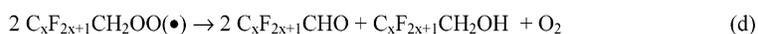
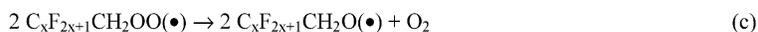
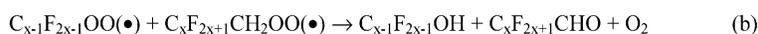


FIGURE 2. Mechanism leading to the production of perfluorinated aldehydes, eqs a and b, and to the odd-chain-length fluorotelomer alcohols, eqs c and d.

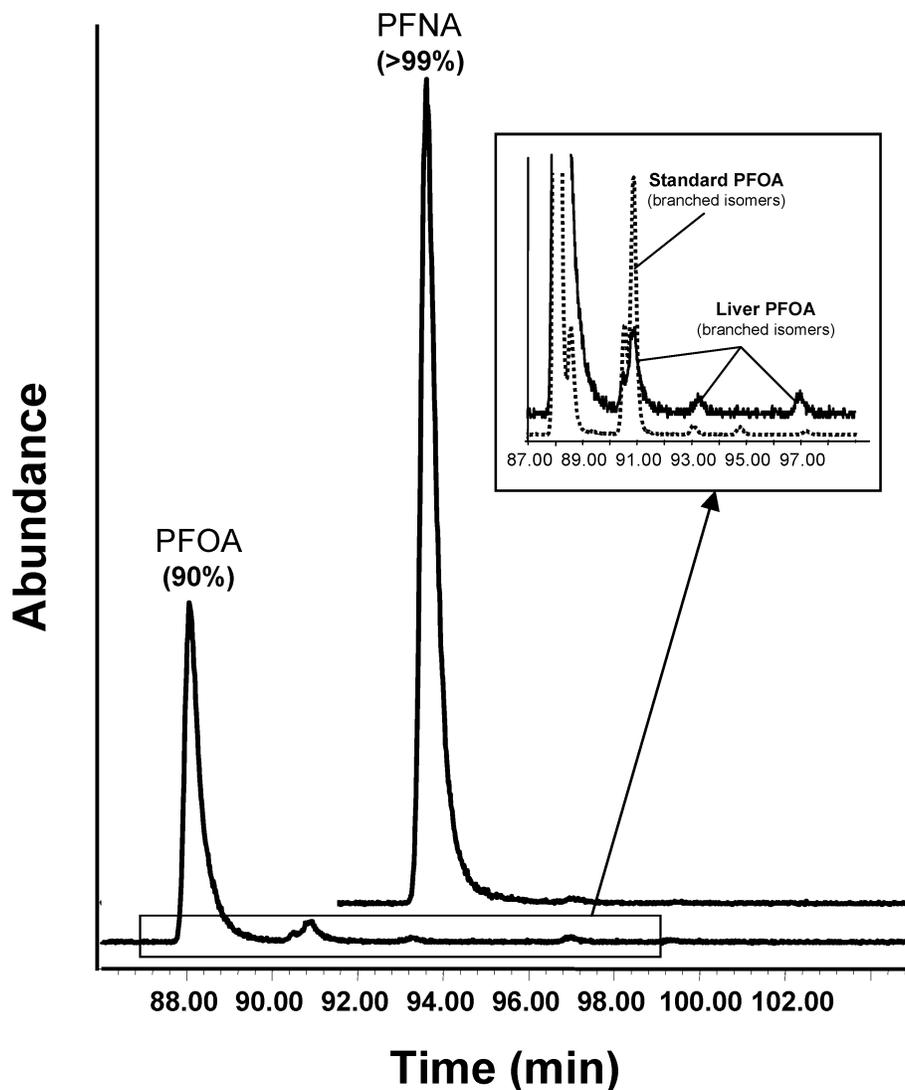


FIGURE 3. Gas chromatogram with mass spectroscopic analysis showing an extracted and derivatized polar bear liver. The inset shows a selective ion comparison between the isomers of an authentic PFOA standard produced electrochemically and PFOA detected in a polar bear liver extract with the largest concentration of isomers observed for each of the extracts. No branched isomers are observed for PFNA. The values in parentheses indicate the percent of acid present in the straight chain form.

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 a PFCA flux in the range 1–100 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.

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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 CF₃CHO suggesting, but not proving, that photolysis of long chain PFALS does not preclude formation of PFCAs via the acyl peroxy + HO₂ reaction route.

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