

Formation of C₇F₁₅COOH (PFOA) and Other Perfluorocarboxylic Acids during the Atmospheric Oxidation of 8:2 Fluorotelomer Alcohol

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Calculations using a three-dimensional global atmospheric chemistry model (IMPACT) indicate that *n*-C₈F₁₇CH₂CH₂-OH (widely used in industrial and consumer products) degrades in the atmosphere to give perfluorooctanoic acid (PFOA) and other perfluorocarboxylic acids (PFCAs). PFOA is persistent, bioaccumulative, and potentially toxic. Molar yields of PFOA depend on location and season, are in the range of 1–10%, and are of the correct order of magnitude to explain the observed levels in Arctic fauna. Fluorotelomer alcohols such as *n*-C₈F₁₇CH₂CH₂OH appear to be a significant global source of persistent bioaccumulative perfluorocarboxylic acid pollution. This is the first modeling study of the atmospheric chemistry of a fluorotelomer alcohol.

1. Introduction

Long-chain perfluorocarboxylic acids (PFCAs, C_{*n*}F_{2*n*+1}COOH where *n* ≥ 6) are highly persistent in the environment and have been observed in fauna from the Great Lakes (1) and the Arctic (2). PFCAs resist degradation via oxidation, hydrolysis, or reduction under biotic and abiotic conditions (3), are bioaccumulative when the perfluorinated chain is more than six carbons in length, and are found in human blood (4). Perfluorooctanoic acid (PFOA) is potentially toxic (5), and the health effects of long-term exposure are the subject of a current Environmental Protection Agency risk assessment.

Other than trifluoroacetic acid (TFA) (6), no natural source of PFCAs has been proposed. The simplest explanation for the ubiquity of PFCAs in biota in remote regions is the presence of widely distributed precursor compounds (presumably of anthropogenic origin) in the atmosphere that degrade to give PFCAs that undergo wet and dry deposition

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within a few days. Fluorotelomer alcohols (FTOHs) have been suggested as PFCA precursor compounds (7, 8). FTOHs are linear fluorinated alcohols with the formula C_{*n*}F_{2*n*+1}CH₂CH₂-OH (*n* = 2, 4, 6, ...). The telomerization process results in even-numbered linear chains, and the alcohols are named according to the number of fluorinated and hydrogenated carbons, e.g., C₈F₁₇CH₂CH₂OH is 8:2 fluorotelomer alcohol (8:2 FTOH). Global production of FTOHs is 12 × 10⁶ kg year⁻¹, and sales are approximately \$700 million annually (9). Fluorotelomer alcohols are volatile, have been observed in the North American atmosphere in significant concentrations (17–135 pg m⁻³) (10, 11), and have an atmospheric lifetime (10–20 days) sufficient for widespread hemispheric distribution (7, 12). C₈F₁₇CH₂CH₂OH (8:2 FTOH) is the most important FTOH and is the subject of the present study.

Figure 1 shows a simplified (photolysis of intermediate aldehydes and formation of thermally unstable alkylperoxy-nitrates are not shown) mechanism for the atmospheric oxidation of 8:2 FTOH. Oxidation of 8:2 FTOH (blue box) is initiated via reaction with OH radicals, which leads to the formation of the perfluoroaldehyde, C₈F₁₇CHO (green box). Oxidation of C₈F₁₇CHO generates C₈F₁₇C(O)O₂ and C₈F₁₇O₂ radicals, which can react with HO₂, CH₃O₂, or NO. As indicated in Figure 1, reactions with HO₂ and CH₃O₂ lead directly, or indirectly, to perfluorocarboxylic acids (red box), while reaction with NO leads to the formation of COF₂.

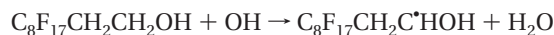
To provide a quantitative assessment of the potential contribution of 8:2 FTOH degradation to the environmental perfluorooctanoic (PFOA, C₇F₁₅COOH) and other perfluorocarboxylic (C_{*x*}F_{2*x*+1}C(O)OH) acid burden, we have constructed a mechanism for the oxidation of 8:2 FTOH and implemented this mechanism in a global atmospheric model. This is the first modeling study of the atmospheric chemistry of a fluorotelomer alcohol. The results indicate that 8:2 FTOH is a significant global source of PFOA and other PFCA pollution.

2. Methodology

The atmospheric oxidation mechanism for 8:2 FTOH given in Table 1 was constructed from literature data. The mechanism and atmospheric models used herein are described briefly here; details are available in the Supporting Information. From the measured atmospheric lifetimes, it has been estimated that a flux on the order of 100–1000 tonnes into the Northern Hemisphere is needed to maintain the observed atmospheric FTOH concentrations (7). In the present work, an annual flux of 1000 tonnes of 8:2 FTOH was assumed.

2.1. Atmospheric Degradation Mechanism for 8:2 FTOH Degradation. The gas-phase atmospheric oxidation mechanism for 8:2 FTOH shown in Table 1 can be broken into the four pieces discussed below.

2.1.1. Atmospheric Oxidation of C₈F₁₇CH₂CH₂OH. The atmospheric degradation of C₈F₁₇CH₂CH₂OH is initiated by reaction with OH radicals. At ambient temperature, this reaction proceeds with a rate constant of 1.1 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ (7, 12). By analogy with reactions of OH with other fluorinated organic compounds, we estimate $k(\text{OH} + \text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OH}) = 3.2 \times 10^{-11} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.



Reaction of OH radicals with 8:2 FTOH proceeds via attack on the CH₂ group α to the OH group. The resulting α-hydroxy alkyl radical reacts with O₂ to give the aldehyde C₈F₁₇CH₂-CHO in 100% yield (8).

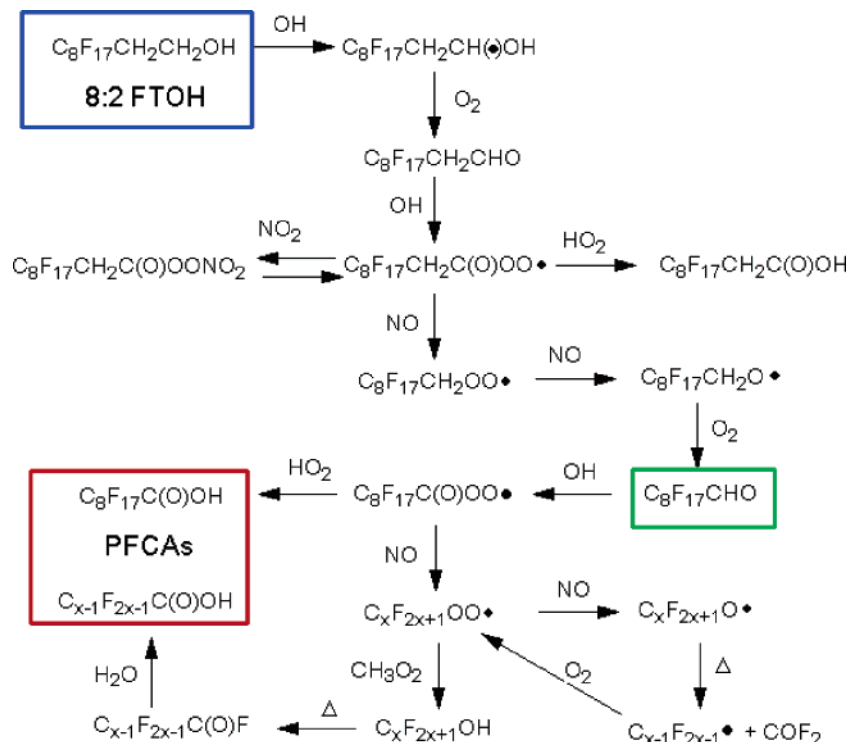


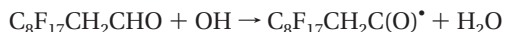
FIGURE 1. Simplified mechanism for the atmospheric degradation of 8:2 FTOH (blue box) illustrating its conversion into $C_8F_{17}CHO$ (green box) and the competition between NO and either HO_2 or CH_3O_2 radicals that limits the formation of perfluorocarboxylic acids (red box).

TABLE 1. Atmospheric Oxidation Mechanism of 8:2 FTOH

reaction	rate
Atmospheric Chemistry of $C_8F_{17}CH_2CH_2OH$	
$C_8F_{17}CH_2CH_2OH + OH \rightarrow C_8F_{17}CH_2CHO$	$3.2 \times 10^{-11} \exp(-1000/T)^a$
Atmospheric Chemistry of $C_8F_{17}CH_2CHO$	
$C_8F_{17}CH_2CHO + OH \rightarrow C_8F_{17}CH_2C(O)OO\cdot$	$1.0 \times 10^{-10} \exp(-1000/T)^a$
$C_8F_{17}CH_2C(O)OO\cdot + NO \rightarrow C_8F_{17}CHO$	$8.1 \times 10^{-12} \exp(270/T)^a$
$C_8F_{17}CH_2C(O)OO\cdot + NO_2 \rightarrow C_8F_{17}CH_2C(O)OONO_2$	$1.1 \times 10^{-11} (T/298)^{-1.0}^a$
$C_8F_{17}CH_2C(O)OONO_2 \rightarrow C_8F_{17}CH_2C(O)OO\cdot + NO_2$	$2.8 \times 10^{16} \exp(-13580/T)^b$
$C_8F_{17}CH_2C(O)OO\cdot + HO_2 \rightarrow \text{products}$	$0.6 \times 4.3 \times 10^{-13} \exp(1040/T)^a$
$C_8F_{17}CH_2C(O)OO\cdot + HO_2 \rightarrow C_8F_{17}CHO + CO_2$	$0.4 \times 4.3 \times 10^{-13} \exp(1040/T)^a$
Atmospheric Chemistry of $C_8F_{17}CHO$	
$C_8F_{17}CHO + OH \rightarrow C_8F_{17}C(O)OO\cdot$	$1.7 \times 10^{-11} \exp(-1000/T)^a$
$C_8F_{17}CHO + h\nu \rightarrow C_8F_{17}O_2$	$\phi = 0.02$
$C_8F_{17}C(O)OO\cdot + NO \rightarrow C_8F_{17}O_2$	$8.1 \times 10^{-12} \exp(270/T)^a$
$C_8F_{17}C(O)OO\cdot + NO_2 \rightarrow C_8F_{17}C(O)OONO_2$	$1.1 \times 10^{-11} (T/298)^{-1.0}^a$
$C_8F_{17}C(O)OONO_2 \rightarrow C_8F_{17}C(O)OO\cdot + NO_2$	$2.8 \times 10^{16} \exp(-13580/T)^b$
$C_8F_{17}C(O)OO\cdot + HO_2 \rightarrow C_8F_{17}COOH(\text{PFNA}^c) + O_3$	$0.10 \times 4.3 \times 10^{-13} \exp(1040/T)^a$
$C_8F_{17}C(O)OO\cdot + HO_2 \rightarrow C_8F_{17}O_2$	$0.90 \times 4.3 \times 10^{-13} \exp(1040/T)^a$
Atmospheric Chemistry of $C_8F_{17}O_2$	
$C_8F_{17}O_2 + NO \rightarrow C_8F_{17}O + NO_2$	$2.8 \times 10^{-12} \exp(300/T)^a$
$C_8F_{17}O_2 + HO_2 \rightarrow C_8F_{17}O + OH + O_2$	$4.1 \times 10^{-13} \exp(750/T)^a$
$C_8F_{17}O_2 + CH_3O_2 \rightarrow C_8F_{17}O + CH_3O$	$2.7 \times 10^{-12} \exp(-470/T)^a$
$C_8F_{17}O_2 + CH_3O_2 \rightarrow C_8F_{17}OH + HCHO$	$1.0 \times 10^{-13} \exp(660/T)^a$
$C_8F_{17}OH \rightarrow C_7F_{15}COOH(\text{PFOA}^d)$	$2.3 \times 10^{-6}^b$

^a Units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. ^b Units of s^{-1} . ^c PFNA = perfluorononanoic acid = $C_8F_{17}COOH$. ^d PFOA = perfluorooctanoic acid = $C_7F_{15}COOH$.

2.1.2. Atmospheric Oxidation of $C_8F_{17}CH_2CHO$. We assume that (i) reaction with OH is the sole atmospheric loss of $C_8F_{17}CH_2CHO$ and (ii) this reaction proceeds at the same rate as $OH + CF_3CH_2CHO$. From the measurements of Sellevåg et al. (13), we derive $k(OH + C_8F_{17}CH_2CHO) = 1.0 \times 10^{-10} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.



The acyl radicals will add O_2 to give acyl peroxy radicals,

$C_8F_{17}CH_2C(O)O_2$. We assume that $C_8F_{17}CH_2C(O)O_2$ radicals react in the atmosphere with NO, NO_2 , and HO_2 with the same rates and mechanisms as the analogous and well-studied reactions involving $CH_3C(O)O_2$ radicals (see the Supporting Information for details).

2.1.3. Atmospheric Oxidation of $C_8F_{17}CHO$. Oxidation of $C_8F_{17}CHO$ is initiated by both reaction with OH radicals and photolysis. Sellevåg et al. have established an upper limit of $\Phi \leq 0.02$ for the photodissociation quantum yield of CF_3CHO in sunlight. We assume $\Phi = 0.02$ for the photodisso-

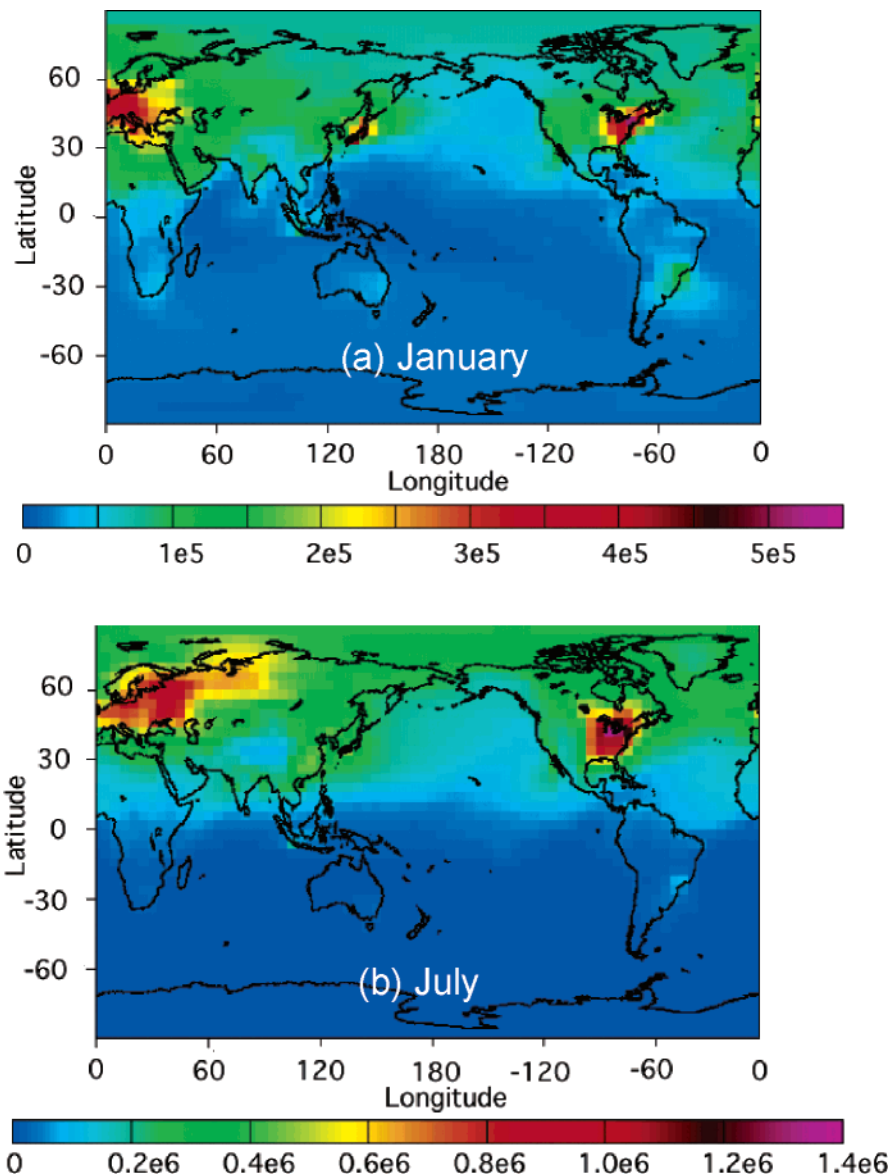


FIGURE 2. Summed concentration of 8:2 FTOH and all of its degradation products at 50 m in altitude for (a) January and (b) July. The color scale extends from (a) 0 to 5.5×10^5 molecule cm^{-3} and (b) 0 to 1.4×10^6 molecule cm^{-3} .

ciation quantum yield of $\text{C}_8\text{F}_{17}\text{CHO}$. From literature data for $\text{C}_x\text{F}_{2x+1}\text{CHO}$ ($x = 1-4$), we derive an estimate of $k(\text{OH} + \text{C}_8\text{F}_{17}\text{CHO}) = 1.7 \times 10^{-11} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This reaction leads to formation of the acylperoxy radical $\text{C}_8\text{F}_{17}\text{C}(\text{O})\text{O}_2$, which is assumed to have the same chemistry as $\text{CH}_3\text{C}(\text{O})\text{O}_2$ radicals. The mechanism of reaction of HO_2 with $\text{C}_8\text{F}_{17}\text{C}(\text{O})\text{O}_2$ radicals (producing $\text{C}_8\text{F}_{17}\text{C}(\text{O})\text{OH}$, PFNA) was assumed to be the same as that for reaction of HO_2 with $\text{C}_3\text{F}_7\text{C}(\text{O})\text{O}_2$ and $\text{C}_4\text{F}_9\text{C}(\text{O})\text{O}_2$ (14).

2.1.4. Atmospheric Fate of $\text{C}_8\text{F}_{17}\text{O}_2$ Radicals. The atmospheric fate of $\text{C}_8\text{F}_{17}\text{O}_2$ will be reaction with NO , NO_2 , HO_2 , and other peroxy radicals (e.g., CH_3O_2). The reactions of $\text{C}_8\text{F}_{17}\text{O}_2$ radicals with NO and HO_2 were assumed to proceed at the same rate as the corresponding reactions of CH_3O_2 radicals. Evidence has been presented that the reaction of $\text{C}_8\text{F}_{17}\text{O}_2$ with alkyl peroxy radicals bearing an α -hydrogen atom leads to the formation of the alcohol $\text{C}_8\text{F}_{17}\text{OH}$, which will undergo heterogeneous decomposition via elimination of HF to give the acid fluoride ($\text{C}_7\text{F}_{15}\text{C}(\text{O})\text{F}$), which undergoes hydrolysis to give the corresponding acid, $\text{C}_7\text{F}_{15}\text{C}(\text{O})\text{OH}$ (PFOA) (8). CH_3O_2 is the most abundant α -hydrogen-containing peroxy radical in the atmosphere. An estimate of the rate constant for the reaction of $\text{C}_8\text{F}_{17}\text{O}_2$ with CH_3O_2 was

obtained from a geometric average of the rates of self-reaction of CF_3O_2 and CH_3O_2 radicals. We assume that PFOA is produced only from reaction of $\text{C}_8\text{F}_{17}\text{O}_2$ with CH_3O_2 and not from the reaction of $\text{C}_8\text{F}_{17}\text{O}_2$ with HO_2 radicals.

2.2. University of Michigan Model (IMPACT). Photochemistry and transport of fluorotelomers were simulated using a three-dimensional (3-D) chemistry/transport model (IMPACT) developed at the Lawrence Livermore National Laboratories and at the University of Michigan (15, 16). IMPACT is a 3-D Eulerian model with 4° latitude by 5° longitude horizontal resolution and 46 vertical layers.

The model has been exercised under the NASA Global Modeling Initiative (GMI, <http://gmi.gsfc.nasa.gov>) using the photochemical representation from the GEOS-CHEM Chemical Mechanism, version 5-07-8, software (17). This includes gas-phase chemistry of all major tropospheric species (CO , reactive nitrogen, representative alkanes and alkenes, and isoprene), with more than 90 species and 300 individual reactions. Emissions of NO_x , CO , and organics are taken from Bey et al. (18). Emission of 8:2 FTOH was added to the model with a global emission rate of 1000 tons per year, with global distribution assumed to be equal to the global distribution of propane from industrial sources.

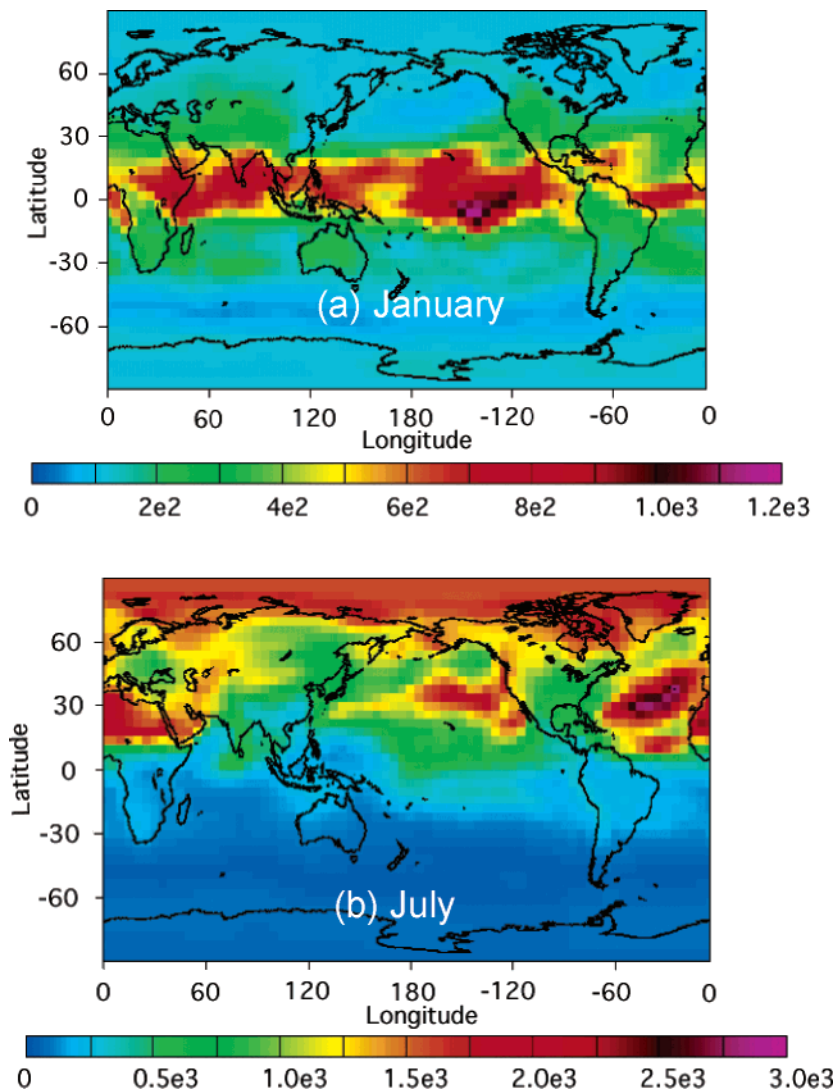


FIGURE 3. Concentration of PFOA (in molecule cm^{-3}) at 50 m in altitude for (a) January and (b) July. The color scale extends (a) from 0 to 1.2×10^3 molecule cm^{-3} and (b) from 0 to 3×10^3 molecule cm^{-3} .

Chemistry, deposition, and transport were included for species formed in the photochemical degradation of 8:2 FTOH. These include the $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHOH}$ radical, $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$, $\text{C}_8\text{F}_{17}\text{CH}_2\text{C}(\text{O})\text{O}_2$, $\text{C}_8\text{F}_{17}\text{CH}_2\text{C}(\text{O})\text{OONO}_2$, $\text{C}_8\text{F}_{17}\text{CH}_2\text{C}(\text{O})\text{OH}$, and $\text{C}_8\text{F}_{17}\text{CH}_2\text{C}(\text{O})\text{OOH}$ (products in Table 1), $\text{C}_8\text{F}_{17}\text{CHO}$, $\text{C}_8\text{F}_{17}\text{C}(\text{O})\text{OO}$, $\text{C}_8\text{F}_{17}\text{C}(\text{O})\text{OONO}_2$, $\text{C}_8\text{F}_{17}\text{C}(\text{O})\text{OH}$ (PFNA), $\text{C}_8\text{F}_{17}\text{O}_2$, $\text{C}_7\text{F}_{15}\text{C}(\text{O})\text{F}$, and $\text{C}_7\text{F}_{15}\text{COOH}$ (PFOA). Photochemical reactions, rates, and yields were all included as shown in Table 1 (where products refers to $\text{C}_8\text{F}_{17}\text{CH}_2\text{C}(\text{O})\text{OH}$ and $\text{C}_8\text{F}_{17}\text{CH}_2\text{C}(\text{O})\text{OOH}$). Photolysis of $\text{C}_8\text{F}_{17}\text{CHO}$ is assumed with a quantum yield of 0.02. $\text{C}_8\text{F}_{17}\text{COOH}$ (PFNA) and $\text{C}_7\text{F}_{15}\text{COOH}$ (PFOA) are removed by wet and dry deposition at rates based on an effective Henry's law coefficient of $2.46 \times 10^3 \text{ mol L}^{-1} \text{ atm}^{-1}$ and a global average dry deposition velocity of 0.19 cm s^{-1} . Lifetimes with respect to wet and dry deposition were 17 and 48 days, respectively, and the lifetime with respect to combined wet and dry deposition was 12 days. The acid, $\text{C}_8\text{F}_{17}\text{CH}_2\text{C}(\text{O})\text{OH}$, and peracid, $\text{C}_8\text{F}_{17}\text{CH}_2\text{C}(\text{O})\text{OOH}$ (labeled products in Table 1), are assumed to be removed through wet and dry deposition at the same rate as PFOA. Because the deposition rates are assumed to be identical, the model ambient concentrations of these species reflect the importance of each species as a terminal product of 8:2 FTOH.

In addition, a tracer species is added to represent other fluoride-containing products resulting from the photochemical degradation of $\text{C}_8\text{F}_{17}\text{O}_2$. This fluoride product tracer

(referred to below as COF_x) is produced by all of the reactions in Table 1 that produce $\text{C}_8\text{F}_{17}\text{O}$ and is removed through wet and dry deposition at the same rate as PFOA. The product tracer is used to determine what fraction of the initial emission of 8:2 FTOH ends up as perfluorocarboxylic acid as opposed to following alternative reaction pathways. The product tracer, when added to the other ambient species and summed wet and dry deposition, provides a complete accounting of the fate of 8:2 FTOH in the model.

3. Results

Figures 2–5 show results obtained using the IMPACT 3-D chemistry/transport model analysis at the University of Michigan. The results suggest that telomers and their degradation products are ubiquitous in the Northern Hemisphere. The sum of 8:2 FTOH and its degradation products (Figure 2) is typically $(0.5\text{--}5) \times 10^3$ molecule cm^{-3} in remote ocean and Arctic locations in the Northern Hemisphere. This is lower than the concentrations in source regions by just a factor of 5 and is consistent with an atmospheric lifetime of 20–40 days for the group as a whole. Telomer species in the remote Northern Hemisphere in the model are one-third primary 8:2 FTOH, one-third long-lived fluorine-containing aldehydes, and one-third terminal reaction products.

Perfluorooctanoic acid (PFOA) (Figure 3) is also ubiquitous in the Northern Hemisphere. Concentrations are often higher

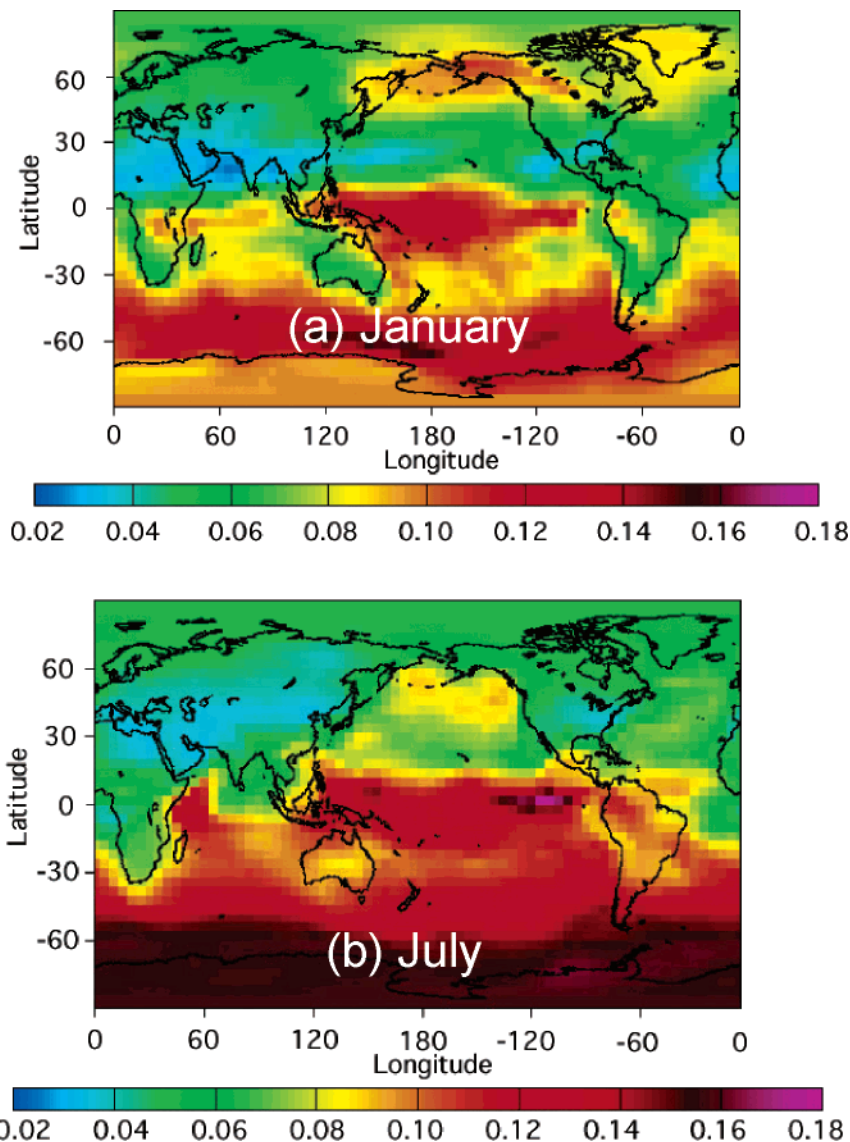


FIGURE 4. Ratio of PFOA to (PFOA + COF_x) at 50 m in altitude for (a) January and (b) July. The color scale extends from 0.02 to 0.18.

at remote locations than in source regions, with the highest values occurring over the Atlantic and Pacific Oceans, North Africa, and the Arctic during the summer. This is consistent with the chemistry described above in the Introduction. Because the reaction of C₈F₁₇O₂ with NO competes with the reaction that forms PFOA, formation of PFOA should decrease with increasing NO_x. Zero-dimensional calculations with chemistry from Table 1 show that the molar yield of PFOA from 8:2 FTOH should be 30% if NO_x is 10 parts per trillion (ppt), 10% if NO_x is 30 ppt, and just 2% if NO_x is 100 ppt. Production of PFOA is therefore suppressed in source regions, which typically have NO_x concentrations of 100 ppt or greater. Perfluorononanoic acid (PFNA, not shown here) shows similar behavior and has concentrations similar to PFOA in the model.

The seasonal behavior of PFOA is noteworthy. During the northern summer, relatively high PFOA concentrations (> 1.5 × 10³ molecule cm⁻³) extend throughout the Arctic, while in the winter concentrations in the Arctic are lower by an order of magnitude. PFOA is lower in winter throughout the Northern Hemisphere at latitudes above 40°. The decrease occurs because photochemical activity is slowed in the northern winter and existing PFOA is removed by deposition.

The molar yield of PFOA from 8:2 FTOH can be assessed by comparing the concentration of PFOA in the model with

that of other termination products. The model includes four termination products: PFOA, PFNA, the sum of C₈F₁₇CH₂C(O)OH and C₈F₁₇CH₂C(O)OOH products in Table 1 (referred to here as FOHp), and the tracer for other products of C₈F₁₇O₂ (COF_x). Because each of these species is removed by deposition at the same rate in the model, the ratio of each to the sum of the four termination products gives the effective molar yield of the species from 8:2 FTOH. The ratio of the species concentrations shows the relative importance of each species as a terminal product for emitted 8:2 FTOH.

The ratio PFOA/(PFOA + COF_x) represents the fraction of C₈F₁₇O₂ radicals that react to give PFOA. As shown in Figure 4, this ratio is typically 0.04–0.08 in the Northern Hemisphere. Fractions are higher (typically 0.10–0.16 and up to 0.18 in the Antarctic) in the Southern Hemisphere where NO_x concentrations are lower. (It should be stressed that 8:2 FTOH concentrations in the Antarctic are extremely low, so while the PFCA yield is relatively high, the absolute magnitude of PFCA formation is extremely low.) The molar yield for PFOA, represented by the ratio PFOA/(all termination products), is somewhat smaller, with typical values of 0.03–0.06 (Figure 5). The fluorine product tracer COF_x is typically the largest termination product, but the miscellaneous acid products (FOHp) are often equally large. The acid products are proportionally more important in northern latitudes during

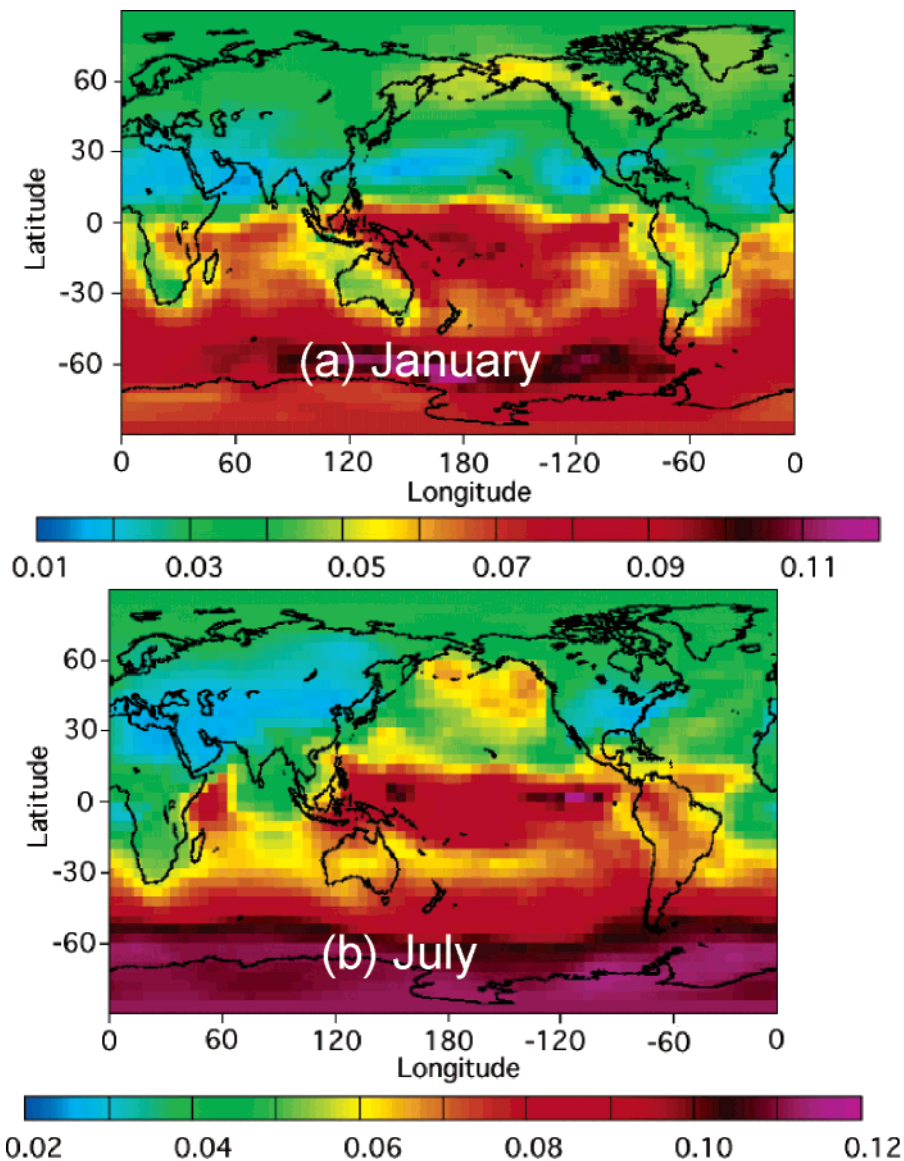


FIGURE 5. Ratio of PFOA to summed termination products at 50 m in altitude for (a) January and (b) July. The color scale extends (a) from 0.01 to 0.12 and (b) from 0.02 to 0.12.

the winter because the lack of sunlight slows the formation rate of species that are produced from longer sequences of reactions. The molar yield of PFNA is similar to that of PFOA (3–6%).

Integrating over the latitude range 65–90° N provides an estimate of 0.4 tonnes year⁻¹ for the PFOA deposition flux to the Arctic. To place this flux into perspective, it can be noted that it is of a similar order of magnitude to the annual arctic loading of persistent organochlorine pesticides such as hexachlorobenzene (1.8 tonnes year⁻¹) (19). Although bioaccumulation factors, spatial variation, and accumulated burdens are also important, it is notable that hexachlorobenzene is detectable in polar bears at a similar concentration to PFCAs (183 ng/g (mean wet weight adipose)) (2). Hence, the results from the present modeling study suggest that the atmospheric degradation of 8:2 FTOH contributes to PFCAs observed in remote locations.

4. Implications for Atmospheric Chemistry

The motivation for the present work was to provide the first quantitative estimate for the possible PFCA yield during the atmospheric oxidation of 8:2 FTOH (C₈F₁₇CH₂CH₂OH). A chemical mechanism describing the atmospheric oxidation

of 8:2 FTOH was constructed from the literature database (section 2.1 and the Supporting Information). The chemical mechanism was implemented in a 3-D global atmospheric model. The results from the model allow three important conclusions to be drawn. First, it seems likely that PFNA, PFOA, and other smaller PFCAs are significant products of the atmospheric oxidation of 8:2 FTOH. On the basis of the model constructed herein, the PFOA yield is approximately 3–6% on a per-emissions basis in the Northern Hemisphere. Second, as a result of 8:2 FTOH oxidation, PFOA is likely to be ubiquitous in the Northern Hemisphere. Third, the yield of PFOA and other PFCAs during the atmospheric oxidation of 8:2 FTOH appears to be of the correct order of magnitude to explain the levels of PFCAs observed in fauna in the Arctic. It should be noted that the chemistry generating PFOA given in the bottom left of Figure 1 will likely occur with similar efficiency for the smaller acids (i.e., C₆F₁₃C(O)H, C₅F₁₁C(O)OH, C₄F₉C(O)OH, etc.). Hence, the smaller acids are likely to be formed in yields similar to that of PFOA.

Finally, we note that it was necessary to estimate the flux of 8:2 FTOH entering the atmosphere and many of the kinetic and mechanistic parameters used in the model. Clearly, further experimental and modeling work is needed to refine

our understanding of the atmospheric photooxidation mechanism of fluorotelomer alcohols. The present modeling results do not prove that the atmospheric oxidation of 8:2 fluorotelomer alcohol is the source of PFCAs observed in remote locations. However, the present modeling results show that with current estimates of chemistry and fluxes the atmospheric oxidation of 8:2 FTOH can provide a quantitative explanation for the presence of PFCAs in remote regions. Given the current interest in the environmental research community regarding the sources and impacts of PFCA pollution, we believe this is an important finding.

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Supporting Information Available

Details of the mechanism and atmospheric model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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