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High-Resolution Atmospheric Modeling of Fluorotelomer Alcohols and Perfluorocarboxylic Acids in the North American Troposphere

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A high spatial and temporal resolution atmospheric model is used to evaluate the potential contribution of fluorotelomer alcohol (FTOH) and perfluorocarboxylate (PFCA) emissions associated with the manufacture, use, and disposal of DuPont fluorotelomer-based products in North America to air concentrations of FTOH, perfluorooctanoic acid (PFOA), and perfluorononanoic acid (PFNA) in North America and the Canadian Arctic. A bottom-up emission inventory for PFCAs and FTOHs was developed from sales and product composition data. A detailed FTOH atmospheric degradation mechanism was developed to simulate FTOH degradation to PFCAs and model atmospheric transport of PFCAs and FTOHs. Modeled PFCA yields from FTOH degradation agree with experimental smog-chamber results supporting the degradation mechanism used. Estimated PFCA and FTOH air concentrations and PFCA deposition fluxes are compared to monitoring data and previous global modeling. Predicted FTOH air concentrations are generally in agreement with available monitoring data. Overall emissions from the global fluorotelomer industry are estimated to contribute approximately 1–2% of the PFCAs in North American rainfall, consistent with previous global emissions estimates. Emission calculations and modeling results indicate that atmospheric inputs of PFCAs in North America from fluorotelomer-based products will decline by an order of magnitude in the near future as a result of current industry commitments to reduce manufacturing emissions and lower the residual fluorotelomer alcohol raw material and trace PFCA product content.

Introduction

Perfluorocarboxylates (PFCAs) have been detected in humans and animals in both urban and remote locations (1, 2). The

observation of PFCAs in the Arctic is unexpected given that they exist as anions in aqueous solutions with pH > 5 (3), have a high affinity for water, and thus are efficiently removed by both wet and dry deposition (4). However, recent studies have shown that the protonated form of perfluorooctanoic acid (PFOA) and the ammonium salt of perfluorooctanoate (APFO) sublime at room temperature (5) and the protonated acid may be subject to long-range atmospheric transport because it has a high Henry's constant and very low water solubility (6).

The contributions of historical and current PFCA sources to concentrations measured in the environment, especially the Arctic, and the mechanisms of PFCA transport through the environment are areas of scientific debate. Two distinct hypotheses have been proposed. The first proposes that PFCAs in remote regions are produced *secondarily* by atmospheric oxidation of one or more volatile precursor substances (7, 8). The second proposes that PFCAs in the Arctic are primarily the result of oceanic transport of PFCAs *directly* released via a variety of industrial processes (9, 10). A recent critical review of the sources, fate, and transport of PFCAs (10) estimated that total historic releases of PFCAs from all sources range from 3200 to 7300 metric tons. Direct releases associated with PFCA manufacture and use were estimated to account for about 95% of total releases. By comparison, indirect releases of PFCAs associated with the degradation of fluorotelomer-based products from 1974 to 2004 were estimated to range between 6 and 130 metric tons, thus representing approximately 1% of total historical releases of PFCAs to the global environment.

Fluorotelomer alcohols (FTOHs) have been proposed as a potential source of PFCAs in remote regions (8). FTOH oxidation in gas-phase smog chamber studies produced a series of PFCAs with yields of 1–10% (8), and the estimated atmospheric FTOH lifetimes are sufficient to make long-range transport likely. FTOHs are raw materials used to make a variety of fluorotelomer-based products (3). Low FTOH concentrations are present as residuals in these products (11). FTOH environmental releases occur both during the manufacture and industrial use of fluorotelomer-based products. In addition to FTOHs, recent smog chamber studies have identified fluorotelomer olefins (12) and N-alkyl perfluoroalkylsulfon-amides (13) and -amidoethanols (14) as additional potential PFCA precursors.

Recently, a three-dimensional global atmospheric chemistry model called IMPACT was used to estimate the yields of PFCAs from the atmospheric gas-phase oxidation of C₈F₁₇-CH₂CH₂OH (8:2 FTOH) (7). The model produced a global yield of 3–6% PFOA per mole of 8:2 FTOH emitted to the air. However, the IMPACT model has a spatial resolution of 4° latitude by 5° longitude (1° is about 100 km at mid-latitudes) which limits the model's ability to resolve sub-continental-scale chemistry effects and transport pathways. Models with higher spatial and temporal resolution provide an enhanced ability to distinguish spatial regions with high and low concentrations of atmospheric nitrogen oxides (NO_x), especially across areas such as the Eastern United States that contain many large NO_x point sources. This is important since PFCA formation via the gas-phase oxidation of FTOH is known to be sensitive to local NO_x concentrations (8). A high-resolution grid also improves the model's ability to describe wind patterns that govern important source-receptor relationships, for example, between sources in the Eastern U.S. and receptors in the Canadian Arctic. Finally, improved model resolution permits more accurate comparisons between modeled concentrations and the results of ambient

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TABLE 1. Comparison of Modeling and Monitoring Results for Global Emissions of 8:2 FTOH^a

source of concentration values		predicted or measured atmospheric concentrations of 8:2 FTOH (pg/m ⁻³)		
		regional: in regions adjacent to point sources	continental: in North American urban areas	remote: in Canadian Arctic
modeling	CAMx	100–1500 ^b	3–250 ^b	<1–6 ^b
	IMPACT	15–60 ^b	5–50 ^b	2–25 ^b
monitoring	Stock et al. (18)	50–200 ^c	1–80 ^c	not measured
	Shoeib et al. (19)	not measured	25–61 ^d	6–26 ^d
	Jahnke et al. (22)	not measured	33–275 ^e	not measured

^a Concentration values from CAMx and IMPACT models have been scaled to reflect estimated global emissions of 150 tons/year 8:2 FTOH.

^b Annual average values estimated from CAMx and IMPACT simulations for one year. ^c The 4-day average concentrations of 8:2 FTOH in a range of North American urban settings (Stock et al.). ^d The 1-day average concentrations of 8:2 FTOH in an arctic transect and in Toronto (Shoeib et al.). ^e The 3.5-day average concentrations of 8:2 FTOH in urban and rural settings in northern Germany (Jahnke et al.).

monitoring. Further discussion of the effects of NO_x chemistry and model resolution on long-range transport of FTOH may be found in the Supporting Information.

Here, we use a high-resolution tropospheric photochemical transport model to study relationships between air emissions, atmospheric reactions, and surface deposition of FTOHs and PFCAs. A detailed FTOH atmospheric degradation chemical mechanism was developed and tested against smog chamber studies (8). This mechanism was incorporated into a photochemical grid model covering continental North America with a 72 by 72-km horizontal grid and a 1 h temporal resolution to explicitly model direct transport and surface deposition of PFCAs and FTOHs within North America and to the North American Arctic. The modeling effort identifies key intermediate products in the atmospheric degradation pathway of FTOHs and quantifies the fraction of FTOH that reacts within the continental “airshed” as well as the fraction that exits to the global troposphere. Finally, the model is used to compare the atmospheric concentrations of FTOHs and PFCAs that result from recent historical emissions and future reduced emissions associated with DuPont fluorotelomer manufacturing, use, and disposal in North America.

Materials and Methods

A detailed chemical mechanism was developed to describe 8:2 FTOH gas-phase atmospheric degradation to intermediate and final products such as small single carbon species (e.g., CO, CF₂O). The mechanism, shown in Figure S2 of the Supporting Information, contains 123 reactions of 41 species and considers reaction pathways not previously included in any other model and is the most complete chemical mechanism presented to date. Where possible, rate constants and product distributions for individual reactions are based on published data. In other cases, we estimated rate constants and product distributions by analogy with similar compounds (15). The knowledge bases relevant to FTOH degradation mechanisms include both hydrocarbon reactions for the hydrocarbon portion of FTOH and hydrofluorocarbon (HFC) reactions.

The chemical mechanism (Figure S2) predicts that gas-phase chemical reaction PFCA yields from FTOH depend upon NO_x concentration. Therefore, atmospheric modeling should be conducted with a model capable of distinguishing high and low NO_x regions. High NO_x regions are associated with major anthropogenic emission sources such as urban areas that are best resolved by high-resolution models. The comprehensive air-quality model with extensions (CAMx) was used to model continental North America with high spatial and temporal resolution. CAMx is a three-dimensional, chemical-transport grid model used for tropospheric ozone, aerosols, air toxics, and related air-pollutants (16) that is being used for North American air-quality planning. CAMx was used here to estimate air concentrations of FTOHs and PFCAs and deposition fluxes of PFCAs throughout North

America. In addition to the 8:2 FTOH degradation pathways considered in the chemical mechanism and modeled using CAMx, longer-chain FTOHs were also simulated by assuming analogy with 8:2 FTOH reactions (see the Supporting Information).

Prevailing westerly winds over North America transported some FTOH releases out of the CAMx modeling domain before they reacted. The fraction of FTOH emissions exiting the domain varies by seasonal wind patterns, oxidant levels, and emission location. FTOH and degradation products transported out of the domain continue to react while circling the globe, and they may return to the domain to react further and/or deposit. To model this recirculation, FTOH and products that exited through the eastern and southern domain boundaries were allowed to continue to react and deposit in a Northern Hemispheric domain, approximated by a box model using the developed chemical mechanism. The FTOH and products were assumed to react for 30 days in the box model and encounter a precipitation event every 5.5 days (17). FTOH and products from the box model were then reintroduced uniformly along the western and northern domain boundaries.

FTOH and PFCA air emissions associated with the production, use, and disposal of DuPont fluorotelomer-based products in North America were estimated. These release estimates were based on production, sales, and measured residual PFCA and raw material FTOH concentrations (11). Two time horizons were modeled: a baseline case using 2004 production and sales data and a future case using the same data but with forecast 2007 residual raw material and impurity profiles. Atmospheric release estimates for both time horizons used in this analysis are shown in Table S1. Estimated 8:2 FTOH emissions from production, use and disposal in North America are 20.2 tons/year for 2004. Extrapolating from market-share, total 8:2 FTOH emissions from all fluorotelomer-based products made, used, and disposed of in North America are estimated to be 50 tons/year, and total global emissions are estimated to be 150 tons/year which is substantially less than the 1000 tons/year of global 8:2 FTOH emissions assumed in a previous modeling study (7) and comparable to the estimate of 40–80 tons/year in a recent review (10). For comparison with monitoring data, the results of CAMx and IMPACT have been scaled to reflect estimated global emissions of 150 tons/year 8:2 FTOH as noted below Table 1. The details of how the emissions inventory was developed are provided in the Supporting Information.

Results and Discussion

Comparison with Previous FTOH Modeling. A previous study used the IMPACT (integrated massively parallel atmospheric chemical transport) model (7). Key model characteristics of IMPACT and CAMx are summarized in Table S2 to facilitate comparison. The CAMx domain encompasses North America while the IMPACT model uses

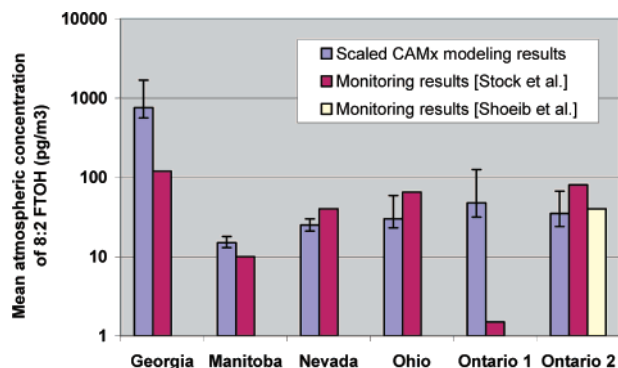


FIGURE 1. Comparison of modeled and monitored atmospheric concentrations of 8:2 FTOH in North America.

a global domain. CAMx has a finer spatial and temporal resolution and uses actual fluorotelomer emissions from product manufacture, use, and disposal distributed on a population-weighted basis. IMPACT assumed 1000 tons/year global 8:2 FTOH emissions distributed proportional to estimated global propane emissions. Both models include only gas-phase FTOH reactions, simulate transport via advection, convection, and diffusion and incorporate PFCA wet and dry deposition. CAMx includes several additional reactions such as CO elimination from the R_fCO radical (where R_f is a perfluoroalkyl group) and peroxide formation from $R_fCH_2CO_2$ and R_fCO_2 radicals.

Predicted Atmospheric FTOH Concentrations. Annual average atmospheric 8:2 FTOH concentrations across North America were calculated for both historical (2004) and future (2007) emissions (Figure S3). Predicted concentrations are highest along the U.S. East Coast due to emissions associated with fluorotelomer product manufacturing and industrial use. Concentrations decreased substantially from 2004 to 2007. Atmospheric 8:2 FTOH concentrations over the rest of continental North America are typically 100 to 1000 times lower than those over the East Coast with annual average concentrations less than 1 pg/m^3 .

Comparison of Predicted and Monitored Atmospheric FTOH Concentrations. In November 2001, air sampling was conducted in six North American cities to investigate the tropospheric FTOH distribution (18). Similar atmospheric monitoring was performed during March 2006 in Toronto (19). To compare CAMx results with these measurements, the continental CAMx results were scaled up by a factor of 2.5 to reflect estimated total fluorotelomer industry 8:2 FTOH emissions in North America where DuPont has an estimated 40% market share. The comparison is shown in Figure 1 and tabulated in Table S3. The November 2001 monitoring data are 4 day mean values during the late fall/early winter while the March 2006 monitoring results are 24 h mean values during the spring. Except for Long Point, ON ("Ontario 1") for which the monitored data appear anomalously low, there is generally good order-of-magnitude agreement between the scaled CAMx model results and the reported atmospheric FTOH monitoring data. The CAMx model tends to overpredict average FTOH in urban locations, but overall, it is in reasonable agreement with the available monitoring data.

Gas and particle phase 8:2 FTOH concentrations of $6\text{--}26 \text{ pg m}^{-3}$ were determined during a July 2005 cruise across the North Atlantic Ocean and through the Canadian Archipelago in the high Arctic (19). The CAMx domain does not extend far enough north to allow direct comparison. However, the predicted values near the northern CAMx domain boundary (latitude 25°N) for both the 2004 and 2007 emission scenarios are on the order of 0.1 pg/m^3 . No significant additional 8:2 FTOH emissions are expected north of the CAMx North American domain. One reason for smaller predicted CAMx

8:2 FTOH concentrations is that, as noted above, we have modeled only part of the 8:2 FTOH North American emission inventory while the monitoring results reflect all FTOH emissions in the Northern Hemisphere. However, an increase of emissions of less than a factor of 10 (i.e., 20.2 tons/year versus 150 tons/year) cannot account for the gap between monitored and modeled 8:2 FTOH concentration which appears to be a factor of up to 2 orders of magnitude.

The spatial 8:2 FTOH concentration patterns predicted by CAMx show a clear relationship between proximity to primary emission sources (e.g., manufacturing locations and population centers) and concentration. The atmospheric 8:2 FTOH concentrations monitored in the Arctic (19) show the lowest 8:2 FTOH concentrations ($<10 \text{ pg m}^{-3}$) in the North Atlantic Ocean and higher concentrations ($>20 \text{ pg m}^{-3}$) in the interior of the Canadian Archipelago and in Norway. The higher readings were likely taken within the Arctic front which is a stable atmospheric regime that forms a reservoir of polluted air that has its origins in the midlatitudes. In July, the climatological boundary of the Arctic front encompasses the region where higher 8:2 FTOH measurements were made in the Canadian archipelago (20), but does not extend southward to the North Atlantic transect. As a result, it appears that measured Arctic concentrations of fluorotelomer alcohols may reflect not only the total global 8:2 FTOH emissions but also an environmental mechanism, which results in increased concentrations as well as reduced spatial and temporal variation.

FTOH atmospheric lifetime lengthens during winter as hydroxyl radical concentrations decrease due to diminished sunlight which causes a modeled seasonal build up of FTOH in the Northern Hemisphere. Additionally, it may be that some FTOH transported from midlatitudes to the Arctic in winter condenses onto snow and remains sequestered during winter conditions. The spring/summer snow thaw may release FTOH and provide a mechanism to enhance summertime FTOH Arctic air concentrations when conditions (e.g., higher OH radical concentrations) are less favorable for long-range transport. The potential for FTOHs to participate in heterogeneous atmospheric processes has not been addressed in this study but is supported by recent monitoring and experimental work (19, 21). Additional monitoring of FTOHs in Arctic air and snow over the entire year would improve the current understanding of their fate and transport mechanisms and make comparisons with modeling more meaningful.

Comparison of Regional, Continental, and Remote Atmospheric FTOH Concentrations. Regional, continental, and Arctic 8:2 FTOH concentrations predicted with CAMx and IMPACT are provided in Table 1 together with available monitoring data. For CAMx, the estimated regional results are directly taken from modeling DuPont emissions in North America, assuming that peak regional concentrations occur around manufacturing sites. At the continental scale, CAMx results have been scaled up as described previously. For estimated global concentrations, the CAMx results have been multiplied by a factor of 7.5 to reflect all global fluorotelomer production, use, and disposal emissions in North America, Asia, and Europe.

At the regional scale, defined as a geographic area within approximately 100 km of a known significant FTOH emission source, CAMx predicts atmospheric concentrations of $100\text{--}1500 \text{ pg m}^{-3}$ (Table 1) while IMPACT predicts $15\text{--}60 \text{ pg m}^{-3}$ (estimated from Figure 2 of ref 6). Both models provide reasonable 8:2 FTOH regional air concentration estimates with CAMx predictions slightly higher and IMPACT results slightly lower than the monitoring results of $50\text{--}200 \text{ pg m}^{-3}$ (18). At the continental scale, representing the broad expanse of central and western North America associated primarily with emissions from fluorotelomer product use and disposal,

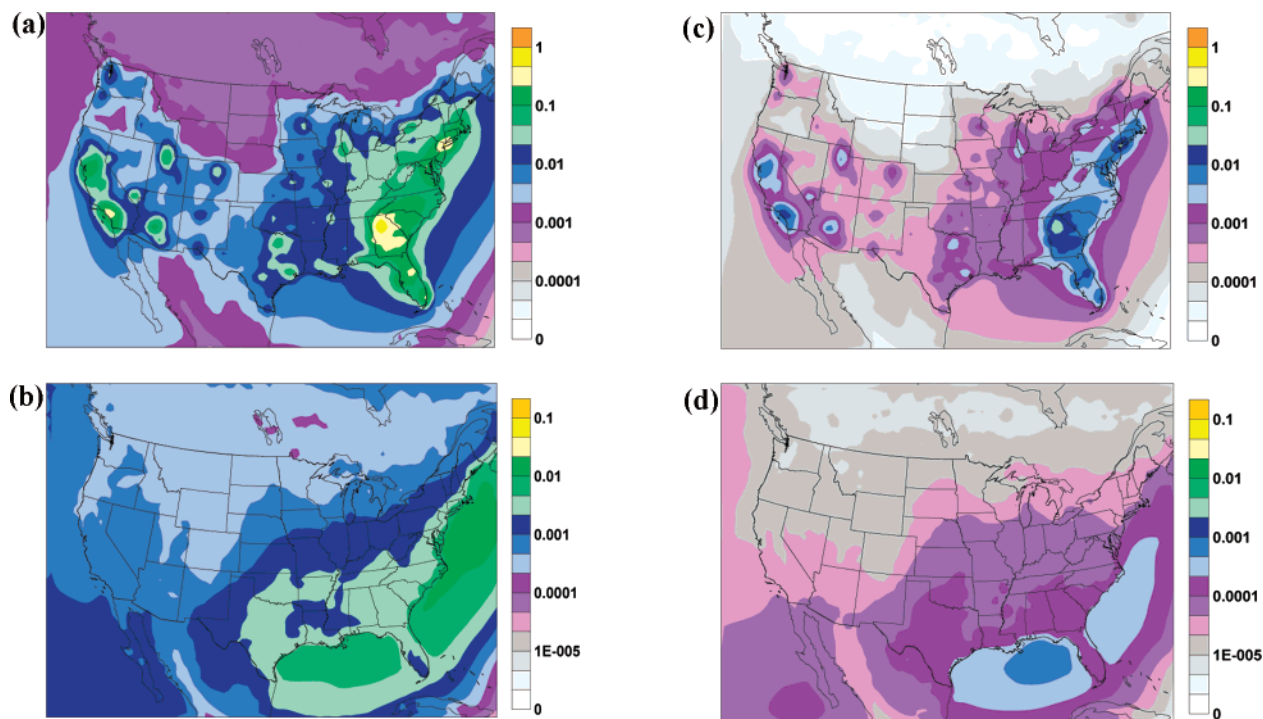


FIGURE 2. Annual average ground-level PFCA air concentrations (pg m^{-3}) from North American air emissions associated with manufacture, use, and disposal of DuPont fluorotelomer-based products. (a) PFOA and (b) PFNA with baseline (2004) release estimates. (c) PFOA and (d) PFNA with future (2007) release estimates.

the predicted atmospheric 8:2 FTOH concentrations are $3\text{--}250 \text{ pg m}^{-3}$ from CAMx and $5\text{--}50 \text{ pg m}^{-3}$ from IMPACT. Measured 8:2 FTOH concentrations reported are $1\text{--}275 \text{ pg m}^{-3}$ (18, 19, 22), in good agreement with both models. Finally, estimated Arctic atmospheric 8:2 FTOH concentrations based on CAMx modeling are low (up to 6 pg m^{-3}) while IMPACT predicts $2\text{--}25 \text{ pg m}^{-3}$ which agrees well with measured summer concentrations of $4\text{--}23 \text{ pg m}^{-3}$.

Comparison of Predicted PFCA Yields with Smog Chamber Studies. The 8:2 FTOH chemical mechanism was tested against smog chamber studies (8). FTOH chemical degradation in the smog chamber was initiated by Cl-atoms rather than OH radicals so Cl-atom reactions were added to the mechanism. The chamber experiments were performed without added NO to maximize the PFCA yields. After 94% of the 8:2 FTOH had reacted, the measured PFCA yields were 1.6, 1.5, 0.32, 0.24, and 0.1% for PFNA, PFOA, perfluoroheptanoic, perfluorohexanoic, and perfluoropentanoic acids, respectively. Our chemical mechanism predicts corresponding PFCA yields of 1.1, 0.9, 0.71, 0.57, and 0.44%. The agreement between our modeled PFCA yields and the smog chamber results is reasonable and supports the use of our mechanism for atmospheric modeling. The CAMx model tendency to predict lower PFNA and PFOA yields than observed in the smog chamber contrasts with a tendency to over predict yields of the lower PFCAs. It is unclear why the yields measured in the smog chamber studies drop sharply between PFOA (1.5%) and perfluoroheptanoic acid (0.32%) since these compounds are understood to form by analogous reactions (Figure S2). This anomaly may warrant further experimental investigation.

Predicted Continental and Hemispherical PFCA Yields.

The seasonal variation of PFOA and PFNA yields predicted by CAMx is provided in Table 2 for the CAMx domain as well as the Northern Hemisphere. Gas-phase FTOH degradation to PFCAs occurs over weeks to months, depending upon season and latitude. As a result, there is global as well as continental scale transport and a varying extent of FTOH degradation to form PFCAs.

TABLE 2. Seasonal Variation in FTOH Reacted and PFCA Yields

season	CAMx domain			Northern Hemisphere		
	8:2 FTOH reacted	PFOA yield	PFNA yield	8:2 FTOH reacted	PFOA yield	PFNA yield
winter (Dec–Feb)	5.4%	0.35%	0.057%	23%	0.80%	0.081%
spring (March–May)	22%	0.66%	0.15%	90%	4.4%	0.49%
summer (June–Aug)	43%	0.85%	0.25%	99%	7.4%	0.45%
autumn (Sept–Nov)	22%	1.1%	0.28%	57%	3.1%	0.50%
annual	26%	0.84%	0.22%	66%	3.9%	0.38%

The fraction of FTOH emitted in North America that reacts within one circuit of the Northern Hemisphere varies seasonally from 23% in winter to 99% in summer (Table 2). Similarly, PFCA yields (PFOA + PFNA) resulting from 8:2 FTOH degradation also vary seasonally from 1% in winter to 8% in summer. Annual PFOA and PFNA yields were 3.9% and 0.38%, respectively. The total annual fraction of 8:2 FTOH consumed was 66%. Recirculation increased the annual PFOA yield from 0.84% within the CAMx domain to 3.9% in the Northern Hemisphere because FTOH degradation products (principally the aldehydes) formed outside the CAMx domain reentered the CAMx domain and reacted to form PFCAs.

PFCA formation from FTOH degradation is highly dependent upon atmospheric NO_x abundance. The time scale for FTOH degradation is on the order of weeks to months and acid yields are highest in low- NO_x areas. Figure S4 in the Supporting Information shows the spatial distribution of PFOA yield within the CAMx modeling domain. The PFOA yield depends on the relative reaction rates of perfluoroacetylperoxy radicals ($\text{C}_8\text{F}_{17}\text{OO}$) with NO and RO_2 radicals (Figure S2). The monthly mean PFOA and PFNA yields for February and July and, for PFOA, is comparable to the IMPACT model results (7). Yield patterns and magnitudes in the two models are roughly similar over the CAMx domain. In July, the lowest

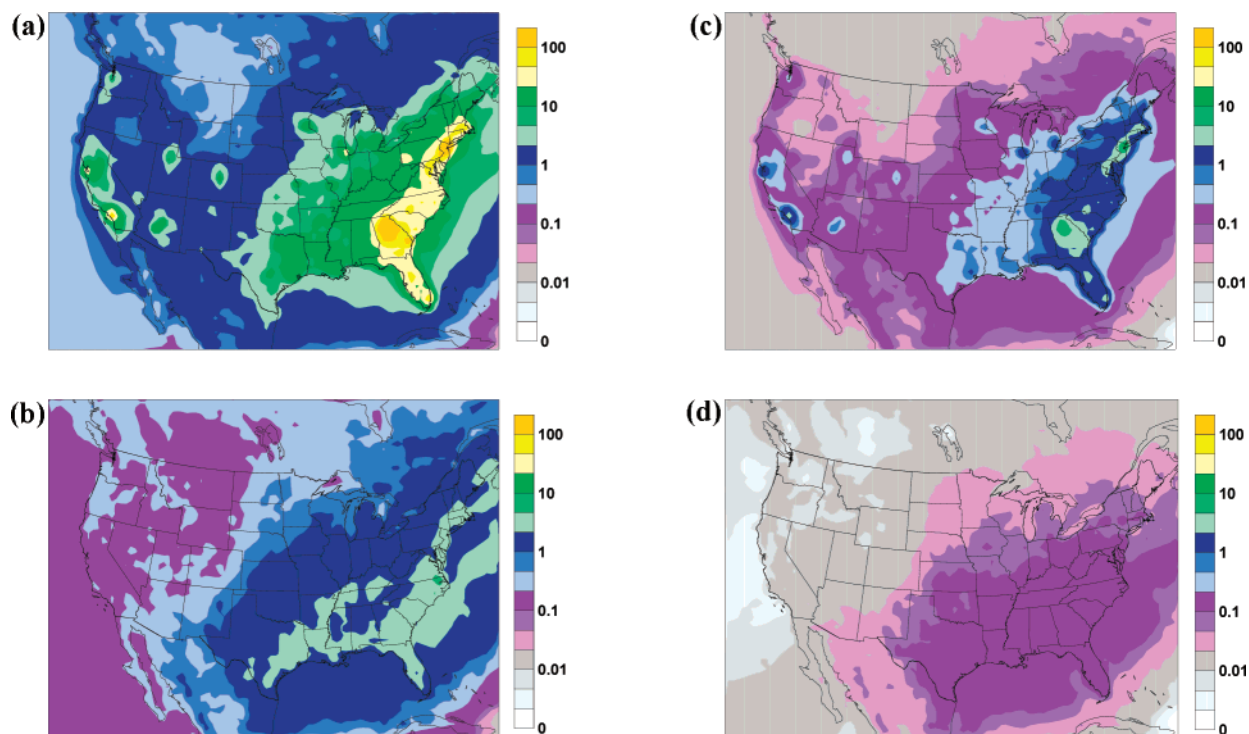


FIGURE 3. Total annual PFCA deposition (ng m^{-2}) from North American air emissions associated with manufacture, use, and disposal of DuPont fluorotelomer-based products. (a) PFOA and (b) PFNA with baseline (2004) release estimates and (c) PFOA and (d) PFNA with future (2007) release estimates.

TABLE 3. Comparison of Modeling and Monitoring of PFCA Deposition in North America

PFCA	source of deposition values	predicted or measured annual deposition fluxes (ng/m^{-2})		
		regional: in eastern U.S., adjacent to point sources	continental: in remainder of continental U.S.	remote: in areas far from significant emission sources
PFOA	modeling: CAMx ^a	30–200	3–100	2–20
	monitoring: Scott et al.	3200–11 000	410–4200	50–300
PFNA	modeling: CAMx ^a	3–10	1–10	0.8–5
	monitoring: Scott et al.	1600–13 000	120–1700	20–250

^a Fluxes calculated by CAMx have been scaled as follows: regional: no scaling, fluxes are assumed to be dominated by local emission sources; continental and remote: increased by 2.5 \times to account for total North American fluorotelomer production.

yields in CAMx are found over the NO_x -rich Ohio Valley. The greater CAMx spatial resolution reveals regional differences more distinctly highlighting yield differences between high- and low- NO_x regimes which are less apparent in IMPACT in winter over the CAMx domain. CAMx and IMPACT yields and patterns are not as close in summer. The reasons for this are unclear.

Predicted Atmospheric PFCA Concentrations. Atmospheric PFOA and PFNA concentrations predicted with CAMx are shown in Figure 2 for the baseline and future emissions. The predicted gas-phase concentrations of PFOA in 2004 are less than 1 pg m^{-3} with reductions of almost 2 orders of magnitude predicted for 2007. Predicted PFNA concentrations are 10–100 times lower than PFOA concentrations in each emission scenario.

A comparison of regional, continental, and Arctic PFOA concentrations in North America predicted by CAMx and IMPACT is provided in Table S4. The scaling methods developed for FTOHs based on market share were applied to the CAMx PFOA results to adjust continental and Arctic concentrations. The two models estimate similar regional and continental atmospheric PFOA concentrations of $0.03\text{--}0.08 \text{ pg m}^{-3}$. IMPACT estimates Arctic PFOA concentrations of 0.15 pg m^{-3} , several orders of magnitude higher than CAMx. This difference is due largely to differences in the assumed

FTOH emissions geographic distribution (see Table S2). IMPACT assumes emissions are distributed proportional to propane emissions whereas CAMx utilizes actual manufacturing and industrial use sites and population-based consumer use and disposal. A lack of PFCA air measurements precludes comparisons of modeled concentrations with monitoring results, but PFCA deposition data are available.

Predicted PFCA Deposition Fluxes and Concentrations in Precipitation. PFCA concentrations in precipitation from nine sites in North America have been reported (23) which can be directly compared to our modeling results. Figure 3 shows the PFOA and PFNA deposition flux from 2004 air emissions associated with the manufacture, use, and disposal of DuPont fluorotelomer-based products in North America. This figure includes direct PFOA and PFNA emissions, secondary PFCA production from FTOH degradation, and both wet and dry PFCA deposition. The pattern of PFOA deposition is a function of the PFOA surface layer concentration as well as regional differences in rainfall. The highest PFOA fluxes are predicted to occur on the Eastern Seaboard of North America. PFNA deposition fluxes are about 10 times lower than PFOA deposition fluxes everywhere in the CAMx domain, and they are about 100 times lower in the mid-Atlantic and Southeastern United States.

PFOA deposition fluxes are generally higher in and downwind of highly populated urban regions and are at least 10 times lower in rural areas. The spatial distribution of PFCA fluxes in precipitation (23) is broadly consistent with our modeled results: the highest average PFOA and PFNA fluxes were seen in urban areas, with the highest fluxes in the mid-Atlantic. The precipitation study did not include samples collected in the Southeastern United States. Consistent with our results, experimentally measured annual average PFCA fluxes were at least an order of magnitude lower in rural areas than in highly populated areas.

Although the spatial distribution of the modeled and measured PFCA deposition fluxes agree reasonably well, the CAMx results are orders of magnitude lower than the precipitation values (23) (Table 3), even though the CAMx results combine wet and dry deposition, whereas the data are just wet deposition. The precipitation monitoring data result in annual PFOA fluxes up to 11 000 ng/m² and PFNA fluxes up to 13 000 ng/m² in regions influenced by local point sources. (see Supporting Information for calculation details). In contrast, the regional estimated PFOA and PFNA fluxes for total North American fluorotelomer production, use and disposal are 50–100 times lower than the precipitation monitoring data. Neither increasing the yield of PFCAs from FTOHs nor increasing the scavenging efficiency (which is already assumed to be 100%) can account for the disparity between the modeled and measured deposition fluxes. A comparison of the observed and modeled values at the regional, continental and remote scales suggests that emissions from the global fluorotelomer industry account for approximately 1–2% of the PFCAs in rainfall. Additional potential sources of atmospheric PFCAs include direct emissions (10) as well as PFCAs formed indirectly from other precursors such as perfluoroalkyl sulfonamido alcohols and amide and fluorotelomer olefins (12–14). This assessment agrees well with the previously published assessment of the environmental sources of PFCAs arising principally from the direct manufacture and use of PFCAs with indirect sources such as FTOH degradation contributing approximately 1% of total global historic PFCA emissions (10).

Implications and Future Work. CAMx provides reasonable estimates of gas-phase 8:2 FTOH concentrations over the North American. The predicted PFOA and PFNA yields and concentrations agree reasonably well with the previously published modeling and monitoring data in regional, continental, and remote settings. However, our results show that deposition fluxes are higher in urban areas than in rural areas, and most of the PFOA deposition in urban areas results from primary PFOA emissions in urban areas. In addition, higher local air concentrations of 8:2 FTOH combine with marginally lower acid yields to result in predicted higher deposition of PFCAs in urban areas. The predicted deposition of PFOA and PFNA is 2 orders of magnitude lower than the North American deposition fluxes determined from precipitation monitoring. Additional atmospheric monitoring studies are needed to improve our understanding of the temporal and spatial distribution of FTOHs, other volatile PFCA precursors, PFCAs and key intermediates such as fluorotelomer acids in both temperate regions as well as in Arctic regions which experience extreme seasonal variation in temperature and sunlight. More comprehensive global modeling of the atmospheric fate of fluorotelomer alcohols is also needed which includes all global sources of emissions, appropriate gas-phase and heterogeneous chemistry, wet and dry deposition of key chemical species, and appropriately high spatial and temporal resolution to reflect local concentrations of key reactants such as OH radicals and NO_x.

Acknowledgments

We thank Brian Scott (Environment Canada) for helpful discussions concerning his monitoring studies of PFCAs in precipitation.

Supporting Information Available

Details describing the CAMx model, emissions estimation methodology, and chemical degradation mechanism as well as additional tabular and pictorial representations of the data presented. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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