Supporting Information

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

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CAMx Model

The current version (version 4.20) of the CAMx model, as publicly released at www.camx.com, was used with the addition of the chemical mechanism for FTOH degradation described below. CAMx is a three-dimensional photochemical grid model meaning that it represents the atmosphere as a three-dimensional array of boxes. For this analysis, each grid box is 72-km square with a depth that varies according to the model layer. The model's vertical resolution is finest near the ground (36 meter surface layer) and extends to the lower stratosphere in 20 layers. Meteorological data for CAMx were developed using the PSU/NCAR Mesoscale Model version 5 (MM5) for calendar year 2002. The MM5 provides CAMx with hourly, gridded data for wind vectors, pressure, temperature, diffusivity, humidity, clouds and rainfall. Emissions of volatile organic compounds (VOCs), nitrogen oxides (NOx), CO, SO₂, NH₃ and aerosols were from the Environmental Protection Agency's 2002 National Emissions Inventory. The CAMx modeling databases were originally developed for current regulatory modeling of visibility and particulate matter in the U.S. Each year-long CAMx simulation was completed in one week using two LINUX personal computers with dual core AMD Athlon processors (1990 MHz). Input data for the CAMx simulations required approximately 50 gigabytes of disk space.

The Role of NOx Chemistry and Model Resolution in the Simulation of FTOH Degradation

NO_x plays a key role in determining the extent to which PFCAs form as FTOHs degrade. The from tropospheric ozone chemistry is that ozone formation switches between sensitivity to volatile organic compound (VOC) or NOx precursors depending upon the VOC/NO_x ratio (see textbooks by Seinfeld and Pandis⁴ or Warneck¹⁷). Transitions from VOC to NOx sensitivity occur at fine spatial scales (a few kilometers) and temporal scales (hour-to-hour) such that ozone models must have fine spatial resolution (less than ~36 km grid) to accurately model ozone chemistry. Similarly, the air modeling for this assessment should be capable of fine spatial will run a gauntlet of high- and low-NOx regions as they traverse the model domain. Their residence time in regions of high or low NOx will determine the likelihood that the FTOH reaction products will proceed down the chemical pathway to PFCA formation. A model with high spatial resolution is well-suited to describe this process, while a lower resolution model will tend to smooth out the ambient NOx distribution, reducing average NOx concentrations. This biases lower-resolution models toward higher PFCA yields, as the FTOH molecule and its products spend more time in a low-NOx environment.

Simulation of FTOH Degradation Outside the CAMx Domain

With the inclusion of recirculation, up to 99% of the emitted 8:2 FTOH degrades within one circuit of the northern hemisphere. After 30 days of chemical processing and rain events, recirculated species are reintroduced to CAMx uniformly along the northern and western boundaries of the domain, according to global circulation patterns.

Emissions Inventory Methodology

DuPont's fluorotelomer-based products were divided into five product categories. For each product class, releases were estimated at each stage of a fluorotelomer-based product's lifecycle

(manufacture, industrial application, consumer use and disposal) based on expected usage of that class of products. For geographical apportionment, manufacturing releases were assumed be released at DuPont fluorotelomer manufacturing facilities. Releases during industrial application were split among thirteen geographical regions in North America based on DuPont sales data. Within each geographical region, the aggregated release estimates were distributed according to population density. Release estimates for consumer use and disposal were distributed according to population density throughout Canada, the United States and Mexico).

Based on the raw ingredients and process chemistry used for manufacturing, the fraction of fluorinated active ingredient and a representative molecular weight profile was determined for each product. The resulting product molecular weight profiles include the following range of fluorocarbon chain lengths: C4, C6, C8, C10, C12, C14 and higher.

Emissions estimates

For each portion of the emissions cycle, separate emissions to air, land and water were estimated. Values for manufacturing emissions were based on data obtained from DuPont manufacturing locations (which are all located in Region 6) while customer, consumer and disposal emissions were based on best estimates obtained from compiling global mass balances of fluorotelomers (see related paper on fluorotelomer sources by Cousins *et al.*, 2006, EST 40(1):32-44).

Two sets of emissions values were developed. Current environmental releases for 2004 to air, land and water represent the historical release patterns for fluorotelomers and their residuals based on documented and estimated release patterns. Future releases, for the years 2007 and beyond, reflect the planned reductions in manufacturing releases as well as reductions in the residual content of products used by customers and consumers.

Total North American emissions from manufacture, use and disposal of fluorotelomer-based products from all sources were estimated by assuming that DuPont emissions represented 40% of total North American emissions. As a result, the predicted atmospheric concentrations of FTOHs and PFCAs were multiplied by a factor of 2.5 to permit comparison of the model predictions with available monitoring data. This correction factor was not applied in the immediate vicinity of major manufacturing locations since these local emissions are typically dominated by the local source.

Total global emissions from manufacture, use and disposal of fluorotelomer-based products from all sources were estimated by assuming that total North American emissions represented one third of global emissions. As a result, the predicted atmospheric concentrations of FTOHs and PFCAs were multiplied by a factor of 2.5x3 = 7.5 to permit comparison of the model predictions with the IMPACT model results.

Emissions calculations

Summaries of DuPont product sales, including sales volume, fractional fluorinated active ingredient, molecular weight distribution and residual content were prepared for 2004 and 2007. Summaries were prepared by region as well as for all of North America; the summaries for all of North America contained information on product cycle, environmental media, product class and chain length.

The emissions values for each region represent the combined releases from manufacturing, customer use, consumer use and disposal for all products sold and used within each region.

Products sold to customers in a specific region are assumed to be disposed of in that same region. The geographic distribution of these products within a region is assumed to be proportional to the distribution of local population, with use and disposal determined on a per capita basis.

A summary of the estimated annual air emissions of PFCAs and FTOHs associated with the production, use, and disposal of DuPont's fluorotelomer-based products in North American for 2004 and 2007 are provided in Table S1.

Methodology used to calculate DuPont fluorotelomer emissions in North America

Annual global sales data for the fluorotelomer-based products of DuPont Chemical Solutions Enterprise (DCSE) are stored in a database maintained by the company. This database was queried to obtain all product sales of fluorotelomer-based products (intermediates, polymers and surfactants) for the USA, Mexico and Canada for the years 1999 through 2005 (year-to-date). North American sales data listing the product name, composition, pounds sold and the customer's name and address were compiled and sales data for the year 2004 were selected, as 2004 was the most recently completed year. Regional sales were compiled for thirteen geographic regions distributed across North America:

Region 1: Northwestern USA (ID, OR, WA)

- Region 2: Southwestern USA (AZ, CA, NV, UT)
- Region 3: North Central USA (ND, NE, MT, SD, WY)
- Region 4: South Central USA (CO, KS, NM, TX, OK, AR, LA, MS, TN, AL)
- Region 5: Midwestern USA
- Region 6: Northeastern USA
- Region 7: Southeastern USA
- Region 8: Mexico
- Region 9: British Columbia, Canada
- Region 10: Central Canada (Alberta, Saskatchewan, Manitoba)
- Region 11: Ontario, Canada
- Region 12: Eastern Canada (Quebec, Newfoundland, Labrador, New Brunswick, Prince Edward)
- Region 13: Northern Canada (Yukon, Northwest Territories, Nunavut) and Alaska



Figure S1: Geographical Regions for Emission Apportionment

Compound	Baseline (2004) Scenario	Future (2007) Scenario
	[kg/yr]	[kg/yr]
8:2 FTOH	20,237	574
10:2 FTOH	10,435	305
12:2 FTOH	3,813	130
14:2 FTOH	2,032	91
PFOA	101	5
PFDA	55	3

Table S1: Estimated annual air emissions of PFCAs and FTOHs associated with the production,use, and disposal of DuPont's fluorotelomer-based products in North America

Model discretization 5° 72 km Latitudinal resolution 5° 72 km Latitudinal resolution 4° 72 km Vertical resolution (bottom layer) Not specified 36 m Vertical resolution 3 hr 1 hr Length of simulation 3 hr 1 hr Temporal resolution 3 hr 1 hr Length of simulation 1 year 1 year Chemical emissions to atmosphere Geographic extent of emissions Global Source of fluorotelomer emissions All sources Biz (12:2: and 14:2 FTOH Perfluorocarboxylic acids emitted None PFOA, PFDA Emission rates Assumed values Emissions Inventory Basis Assumed values Emissions Inventory Historical rates (2004) 3:2 FTOH 1,000 tonnes/yr 8:2 FTOH 1,000 tonnes/yr 0 tonnes/yr Other FTOHs Not modeled 0.6 tonnes/yr 0:tonnes/yr 0.2 tonnes/yr 0.2 tonnes/yr PFCAs Not modeled 0.5 tonnes/yr Geographic distribution of Assumed same as Gas phase	Model characteristics	IMPACT model used by Wallington et al	CAMx model used by Yarwood et al
Longitudinal resolution 5° 72 km Latitudinal resolution 4° 72 km Latitudinal resolution 4° 72 km Vertical resolution 3 hr 1 hr Length of simulation 1 year 1 year Chemical emissions to atmosphere Global North America Geographic extent of emissions Global North America Fluorotelomer alcohols emitted 8:2 FTOH 8:2,10:2,12:2 and 14:2 FTOH Perfluorocarboxylic acids emitted None PFOA, PFDA Emission rates Assumed values Emissions Inventory Basis Assumed values Emissions Inventory Historical rates (2004) 1,000 tonnes/yr 0 tonnes/yr S:2 FTOH 1,000 tonnes/yr 0 tonnes/yr Other FTOHs Not modeled 0.6 tonnes/yr Other FTOHs Not modeled 0.5 tonnes/yr Developed from geographic distribution of Assumed same as Developed from <	Model discretization		
Latitudinal resolution(40 H 4")72 kmVertical resolution (bottom layer)Not specified36 mVertical layers46, covering 20 km20, covering 14 kmTemporal resolution3 hr1 hrLength of simulation1 year1 yearChemical emissions to atmosphereGeographic extent of emissionsGlobalFluorotelomer alcohols emittedNonePerfluorocarboxylic acids emittedNonePerfluorocarboxylic acids emittedNoneEmission ratesAssumed valuesBasisAssumed valuesBasisAssumed valuesPerfluorocarboxylic acids emittedNonePFCAs0 tonnes/yrOther FTOHs0 tonnes/yrQitter FTOHsNot modeledOther FTOHsNot modeledPFCAs0 tonnes/yrPFCAs0 tonnes/yrPFCAs0 tonnes/yrPFCAs0 tonnes/yrCoditioner emissionspropanemulated chemical reaction pathwaysGas phasePhase for all FTOH reactions Additional fluorotelomer pathwaysGas phaseN/AN/Aadvection and diffusionImPACTincludedVertical and horizontal advection and diffusionSimulated transport and deposition mechanismsVertical and horizontal advection and diffusionTransportVertical and horizontal advection and diffusionDepositionWet and dry deposition	Longitudinal resolution	5° (395 km at 45°N)	72 km
Vertical resolution (bottom layer) Vertical layersNot specified 46, covering 20 km36 m 20, covering 14 kmTemporal resolution 	Latitudinal resolution	4° (444 km)	72 km
Temporal resolution Length of simulation3 hr 1 year1 hr 1 yearChemical emissions to atmosphere 	Vertical resolution (bottom layer) Vertical layers	Not specified 46, covering 20 km	36 m 20, covering 14 km
Chemical emissions to atmosphere Geographic extent of emissionsGlobalNorth America (25° to 60°N, 60° to 135°W) DuPont North America 8:2 FTOHSource of fluorotelomer emissions Fluorotelomer alcohols emittedAll sources 8:2 FTOHNorePEOA, PEDAPerfluorocarboxylic acids emitted Emission rates BasisNonePEOA, PEDABasisAssumed valuesEmissions InventoryHistorical rates (2004) 8:2 FTOH1,000 tonnes/yr 	Temporal resolution Length of simulation	3 hr 1 year	1 hr 1 year
Geographic extent of emissions Global North America Source of fluorotelomer emissions All sources (25° to 60°N, 60° to 135°W) Source of fluorotelomer alcohols emitted 8:2 FTOH 8:2,10:2,12:2 and 14:2 FTOH Perfluorocarboxylic acids emitted None PFOA, PFDA Emission rates Assumed values Emissions Inventory Historical rates (2004) 1,000 tonnes/yr 20 tonnes/yr S2 FTOH 1,000 tonnes/yr 20 tonnes/yr Other FTOHs 0 tonnes/yr 0.2 tonnes/yr PECAs 0 tonnes/yr 0.2 tonnes/yr Future rates (2007) Not modeled 0.6 tonnes/yr S2 FTOH Not modeled 0.5 tonnes/yr Other FTOHs Not modeled 0.5 tonnes/yr PECAs Not modeled 0.6 tonnes/yr Developed from manufacturing and use data Simulated chemical reaction pathways N/A N/A Phase for all FTOH reactions Gas phase 0 coleimination from R _i CO Additional fluorotelomer pathways N/A N/A 0 coleimination from R _i CO IMPACTincluded Vertical and horizontal chemistry <	Chemical emissions to atmosphere		
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Basis Assumed values Emissions Inventory Historical rates (2004) 1,000 tonnes/yr 20 tonnes/yr 0 ther FTOHs 0 tonnes/yr 20 tonnes/yr PFCAs 0 tonnes/yr 0.2 tonnes/yr 0 ther FTOHs 0 tonnes/yr 0.2 tonnes/yr 0 ther FTOHs 0 tonnes/yr 0.2 tonnes/yr 0 ther FTOHs Not modeled 0.6 tonnes/yr 0 ther FTOHs Not modeled 0.5 tonnes/yr 0 ther FTOHs Not modeled 0.5 tonnes/yr 0 ther FTOHs Not modeled << 0.1 tonnes/yr	Perfluorocarboxylic acids emitted	None	PFOA, PFDA
8:2 FTOH 1,000 tonnes/yr 20 tonnes/yr 8:2 FTOH 0 tonnes/yr 16 tonnes/yr Other FTOHs 0 tonnes/yr 0.2 tonnes/yr PFCAs 0 tonnes/yr 0.2 tonnes/yr Future rates (2007) 8:2 FTOH Not modeled 0.6 tonnes/yr Other FTOHs Not modeled 0.5 tonnes/yr Other FTOHs Not modeled 0.5 tonnes/yr Other FTOHs Not modeled << 0.1 tonnes/yr	Basis Historical rates (2004)	Assumed values	Emissions Inventory
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PFCAs 0 tonnes/yr 0.2 tonnes/yr Future rates (2007) 8:2 FTOH Not modeled 0.6 tonnes/yr Other FTOHs Not modeled 0.5 tonnes/yr PFCAs Not modeled << 0.1 tonnes/yr	Other FTOHs	0 tonnes/yr	16 tonnes/yr
Big Signal ated transport and deposition mechanisms Not modeled 0.6 tonnes/yr Not modeled 0.5 tonnes/yr Other FTOHs Not modeled << 0.1 tonnes/yr	PFCAs	0 tonnes/yr	0.2 tonnes/yr
Other FTOHs Not modeled 0.5 tonnes/yr PFCAs Not modeled 0.5 tonnes/yr Geographic distribution of Assumed same as Developed from fluorotelomer emissions propane manufacturing and use data Simulated chemical reaction pathways N/A Beographic distribution from RrCO Phase for all FTOH reactions Gas phase Gas phase Additional fluorotelomer pathways N/A N/A in CAMx compared to N/A Developed formation from RrCO IMPACTincluded Sensitivity test of aldehyde hydrate chemistry Sensitivity test of aldehyde hydrate chemistry Vertical and horizontal advection and diffusion Deposition Wet and dry deposition Wet and dry deposition	8.2 FTOH	Not modeled	0.6 toppes/vr
PFCAsNot modeled<< 0.1 tonnes/yrGeographic distribution of fluorotelomer emissionsAssumed same as propaneDeveloped from manufacturing and use dataSimulated chemical reaction pathways Phase for all FTOH reactions Additional fluorotelomer pathwaysGas phase N/Aa)In CAMx compared to IMPACTincludedN/Aa)CO elimination from R ₁ CO radicalIMPACTincludedSensitivity test of aldehyde hydrate chemistryb)Peroxide formation from R ₁ CH ₂ CO ₂ and R ₁ CO ₂ radicalsSimulated transport and deposition mechanisms TransportVertical and horizontal advection and diffusion Wet and dry depositionVertical and horizontal advection and diffusion Wet and dry deposition	Other FTOHs	Not modeled	0.5 tonnes/yr
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IMPACTincluded b) Peroxide formation from RfCH2CO2 and RfCO2 radicals b) Peroxide formation from RfCH2CO2 and RfCO2 radicals c) Sensitivity test of aldehyde hydrate chemistry Simulated transport and deposition mechanisms chemistry Transport Vertical and horizontal advection and diffusion Deposition Wet and dry deposition	Additional fluorotelomer pathways	N/A	a) CO elimination from R _f CO
Simulated transport and deposition mechanisms radicals Transport Vertical and horizontal advection and diffusion Deposition Wet and dry deposition	IMPACTincluded		b) Peroxide formation from $R_fCH_2CO_2$ and R_fCO_2
C) Sensitivity test of aldehyde hydrate chemistry Simulated transport and deposition mechanisms chemistry Transport Vertical and horizontal advection and diffusion Deposition Wet and dry deposition			radicals
Simulated transport and deposition mechanismsTransportVertical and horizontal advection and diffusionDepositionWet and dry deposition			c) Sensitivity test of aldehyde hydrate chemistry
Deposition Wet and dry deposition Wet and dry deposition	Simulated transport and deposition Transport	<i>mechanisms</i> Vertical and horizontal	Vertical and horizontal
	Deposition	Wet and dry deposition	Wet and dry deposition

Table S2. Comparison of Model Characteristics of IMPACT and CAMx

Location	CAMx (1) (pg/m3)	Monitoring (2) (pg/m3)	Monitoring (3) (pg/m3)
Georgia	755	130	
Manitoba	15	10	
Nevada	25	40	
Ohio	30	65	
Ontario 1	48	1	
Ontario 2	35	80	
Ontario 3	50		40

Table S3. Comparison of modeled and monitored atmospheric concentrations of 8:2 FTOH

Notes: (1) CAMx results have been scaled by a factor of 2.5X to account for total industry emissions in North America

- (2) Data of Stock et al., Env Sci & Tech 2006, 38 (4) 991-996.
- (3) Data of Shoeib et al., Env Sci & Tech 2006, 40 (24) 7577-7583.

Source of co	ncontration	Predicted or measured	atmospheric concentra	tions of PFOA (pg/m3)
val	les	Regional: In regions adjacent to point sources	Continental: In remainder of continental USA	Remote: In Canadian Arctic
Modeling	CAMx	0.04 - 0.36	0.01 - 0.09	< 0.001 - 0.003
wodening	IMPACT	0.03 - 0.08	0.03 - 0.08	0.01 - 0.15

Table S4. Comparison of modeling results for atmospheric concentrations of PFOA

Concentration values from CAMx have been scaled as follows:

regional: no scaling, concentrations are assumed to be dominated by local emission sources continental: increased to 50 t/yr (2.5X) to account for total North American fluorotelomer production remote: increased to 150 t/yr (7.5X) to account for total global fluorotelomer production

Concentration values from IMPACT have been scaled as follows:

all values: decreased to 150 t/yr (0.15X) to account for total global fluorotelomer production

Methodology used to calculate PFCA deposition from data of Scott et al. 2006

In Table 3 of the Scott *et al.* (*Environ. Sci. Technol.* **2006** 41(23), 7167-7174) monitoring study, average PFCA fluxes in precipitation are reported for a series of locations across North America. The mean flux of PFOA and PFNA for each location were multiplied by the number of samples to obtain a cumulative yearly deposition for each PFCA. The results of these calculations are provided in Table 5 of this paper.

Detailed Chemical Mechanism

Species names follow the naming convention for 8:2 FTOH, or 82OH, where "8" is the number of fluorinated carbon atoms and "2" is the number of non-fluorinated (generally hydrogenated or oxygenated) carbon atoms. Thus, PFOA is denoted as 71CA and perfluorononanoic acid (PFNA, $CF_3(CF_2)_7COOH$) is denoted 81CA. The mechanism follows the scheme outlined by Ellis et al. (*Environ. Sci. Technol.* **2004** 38(12), 3316-3321), with some significant differences. For example, CO elimination from perfluoroacyl radicals is included.

The top portion of the chemical mechanism describes the degradation of the hydrocarbon portion of 8:2 FTOH by OH radical and photolysis reactions. PFNA can be formed by reaction of a perfluorinated peroxyacyl radical (81RO3) with an HO₂ radical. PFOA can be formed via reaction of a perfluorinated peroxy radical (80RO2) with an RO₂ radical (e.g., CH₃O₂). The peroxy radical reactions leading to PFNA and PFOA formation from 8:2 FTOH both have analogues in atmospheric hydrocarbon chemistry and they compete against reactions with NO that do not form PFCA. Consequently, the yields of PFCA from FTOH degradation will depend upon the relative abundances of peroxy radicals and NO in the atmosphere. Degradation of the perfluorinated backbone of 8:2 FTOH proceeds by an "unzipping" sequence of radical reactions producing CF₂O and potentially smaller PFCAs (61CA, 51CA, etc.) by reactions analogous to those that form PFOA (71CA).

In addition to the 8:2 FTOH considered in the chemical mechanism and modeled using CAMx, there are longer-chain FTOHs associated with DuPont fluorotelomer-based products that are capable of forming PFCAs (i.e., 10:2, 12:2 and 14:2 FTOH). These compounds were considered in the analysis by analogy to the shorter chain 8:2 FTOH. For example, the proposed chemical mechanism predicts conversion of the 8:2 FTOH to form PFCAs shorter than PFOA and PFNA (e.g., 61CA, 51CA, etc.). The 10:2 FTOH was assumed to form the 71CA (PFOA) with the same yields as the 8:2 FTOH formed the 51CA, and this yield was applied to the total release of the 10:2 FTOH to determine the contribution of the 71CA (PFOA) from the 10:2 FTOH. This process was repeated for all FTOH/PFCA combinations.

Table S5. Chemical mechanism for the OH-radical initiated atmospheric chemical degradation of 8:2 fluorotelomer alcohol (820H).

Notes	1,5	1,5	7,8	7	2,3	2,3	2	2,6	2	2,6	7	4	7,2	1,5	1,5	2	1,4	7,9	=k4	=k5	=k6	=k7	=k8, 6	2,5,6	2,4,5,6	7	4,5	4,5	=k28	2,4,5,6	2,4,5,6	2,4,5,6	2,4,5,6	2,4,5,6	=k28	2,4,5,6	2,4,5	=k31	=k34	=k36	=k37
E _a /R ^(C)	-350	0	N/A	980	N/A	N/A	290	500	910	563	0	190	N/A	-350	-500	0	0	N/A	980	N/A	N/A	290	500	500	510	300	0	500	500	555	500	605	555	555	500	500	500	500	555	500	500
k _{2a8} ^(B)	9.98E-13	3.60E-12	Photolysis	1.40E-11	1.05E-11	5.20E-04	2.00E-11	1.10E-11	3.80E-12	3.33E-12	1.30E-11	2.52E-12	Photolysis	1.02E-13	5.03E-13	5.10E-12	2.51E+07	Photolysis	1.40E-11	1.05E-11	5.20E-04	2.00E-11	1.10E-11	1.20E-12	1.51E-12	1.00E-11	1.00E+04	1.60E-12	1.60E-12	3.51E-12	1.87E-12	4.70E-12	3.51E-12	3.64E-12	1.60E-12	1.87E-12	2.10E-12	1.87E-12	3.64E-12	1.87E-12	2.10E-12
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				0.40															0.70																						
				+															+																						
				81R2															81R2													HO2	80R2	71CA					61CA		
				0.40															0.70													1.00		0.33					0.33		
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	Ĥ		00	03		Ő		81R		81A	О́Н	О́Н	О́Н	Я			8	000	03		Ô		80R	НО	80R		Ū.		80R	81A	80R	81A	Я	Ю́Н		80R		81R	О́Н	80R	80R
				0.20				06.0		0.80									0.20				0.90		0.67							0.50	06.0	0.67					0.67		
	+		+	+		+		+		+	+	+	+	+			+	+	+		+		+	+	+		+		+	+	+	+	+	+		+		+	+	+	+
cts	82AL	82R3	81R2	82CA	82PN	82R3	81R2	82CA	81PX	810H	81AL	81AL	81AL	81AL	81RO	81R3	80R2	80R2	81CA	81PN	81R3	80R2	81CA	80RO	71CA	80RO	70R2	81R2	81R2	81R2	81R2	810H	81AL	81AL	80R2	80R2	80RO	70RO	70RO	70RO	70RO
Produ				0.20				0.10		0.20									0.20				0.10		0.33			2.00				0.50	0.90		2.00		2.00		0.67		
	Ш	Ш	Ш	Ш	II	Ш	II	Ш	Ш	П	П	П	П	П	П	П	Ш	Ш	Ш	П	П	П	Ш	II	П	П	Ш	П	II	II	II	II	П	II	II	П	П	П	П	II	Ш
	Ы	НО		HO2	NO2		Ŋ	X02	HO2	X02	No	НО		НО	НО	02			HO2	NO2		0N N	X02	HO2	X02	No		82R3	81R3	81R2	80R2	81R2	81R3	80R2	81R3	80R2	80R2	82R3	81R2	81R3	80R2
nts ^(A)	+	+		+	+		+	+	+	+	+	+		+	+	+			+	+		+	+	+	+	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+
Reactar	820H	82AL	82AL	82R3	82R3	82PN	82R3	82R3	81R2	81R2	81R2	81PX	81PX	810H	81AL	81RO	81RO	81AL	81R3	81R3	81PN	81R3	81R3	80R2	80R2	80R2	80RO	82R3	82R3	82R3	82R3	81R2	81R2	81R2	81R3	81R3	80R2	70R2	70R2	70R2	70R2
	-	2	e	4	5	9	7	8	6	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41

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	Reac	tants	(A)		Ē	roducts											$k_{298}^{(B)}$	$E_{a}/R^{(C)}$	Notes
42	70R2	+	. 70R	2	- 2.	00 7	ORO										2.10E-12	500	=k37
43	60R2	+	. 82R	" "		9	10RO	+		81R2							1.87E-12	500	=k31
44	60R2	+	. 81R	2	 	67 6	ORO	+	0.67	HO2	+	81AL	+	0.33	51C	A.	3.64E-12	555	=k34
45	60R2	+	· 81R	" "		9	10RO	+		80R2							1.87E-12	500	=k36
46	60R2	+	. 80R	" "	μ	9	10RO	+		80RO							2.10E-12	500	=k37
47	60R2	+	- 70R	" "	μ	9	10RO	+		70RO							2.10E-12	500	=k37
48	60R2	+	. 60R	2	i. "	00 6	10RO										2.10E-12	500	=k37
49	50R2	+	. 82R	" "	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	ŝ	ORO	+		81R2							1.87E-12	500	=k31
50	50R2	+	· 81R	2		67 5	ORO	+	0.67	HO2	+	81AL	+	0.33	41C	A.	3.64E-12	555	=k34
51	50R2	+	. 81R	" "		ŝ	ORO	+		80R2							1.87E-12	500	=k36
52	50R2	+	. 80R	2		ŝ	ORO	+		80RO							2.10E-12	500	=k37
53	50R2	+	. 70R	2		5	ORO	+		70RO							2.10E-12	500	=k37
54	50R2	+	. 60R	2	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	S	ORO	+		60RO							2.10E-12	500	=k37
55	50R2	+	. 50R	2	". "	00 5	ORO										2.10E-12	500	=k37
56	40R2	+	. 82R	" "	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	4	ORO	+		81R2							1.87E-12	500	=k31
57	40R2	+	. 81R	2	 	67 4	ORO	+	0.67	HO2	+	81AL	+	0.33	31C	A.	3.64E-12	555	=k34
58	40R2	+	· 81R	" "		4	ORO	+		80R2							1.87E-12	500	=k36
59	40R2	+	. 80R	2		4	ORO	+		80RO							2.10E-12	500	=k37
60	40R2	+	. 70R	2		4	ORO	+		70RO							2.10E-12	500	=k37
61	40R2	+	. 60R	2		4	ORO	+		60RO							2.10E-12	500	=k37
62	40R2	+	. 50R	2		4	ORO	+		50RO							2.10E-12	500	=k37
63	40R2	+	. 40R	2	i.	00 4	ORO										2.10E-12	500	=k37
64	30R2	+	. 82R	" "	ш	e	10RO	+		81R2							1.87E-12	500	=k31
65	30R2	+	. 81R	2		67 3	10RO	+	0.67	HO2	+	81AL	+	0.33	21C	A.	3.64E-12	555	=k34
66	30R2	+	. 81R	" "	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	с С	10RO	+		80R2							1.87E-12	500	=k36
67	30R2	+	. 80R	2	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	с С	10RO	+		80RO							2.10E-12	500	=k37
68	30R2	+	. 70R	2		с С	10RO	+		70RO							2.10E-12	500	=k37
69	30R2	+	. 60R	" "	μ	e	10RO	+		60RO							2.10E-12	500	=k37
70	30R2	+	. 50R	2		с С	10RO	+		50RO							2.10E-12	500	=k37
71	30R2	+	- 40R	" "	μ	e	10RO	+		40RO							2.10E-12	500	=k37
72	30R2	+	· 30R	" "	i.	00 3	10RO										2.10E-12	500	=k37
73	20R2	+	- 82R	" "	μ	2	ORO	+		81R2							1.87E-12	500	=k31
74	20R2	+	· 81R	" "	ö	67 2	ORO	+	0.67	HO2	+	81AL	+	0.33	110	A	3.64E-12	555	=k34
75	20R2	+	· 81R	" "	μ	2	ORO	+		80R2							1.87E-12	500	=k36
76	20R2	+	· 80R	" "	μ	2	ORO	+		80RO							2.10E-12	500	=k37
77	20R2	+	- 70R	" "	μ	7	ORO	+		70RO							2.10E-12	500	=k37
78	20R2	+	. 60R	2	ш	0	ORO	+		60RO							2.10E-12	500	=k37
79	20R2	+	. 50R	2		0	ORO	+		50RO							2.10E-12	500	=k37
80	20R2	+	. 40R	2		0	ORO	+		40RO							2.10E-12	500	=k37
81	20R2	+	. 30R	2		0	ORO	+		30RO							2.10E-12	500	=k37
82	20R2	+	. 20R	2	-	00 2	ORO										2.10E-12	500	=k37
83	10R2	+	. 82R	" "		-	ORO	+		81R2							1.87E-12	500	=k31
84	10R2	+	- 81R	" "		67 1	ORO	+	0.67	НО2	+	81AL	+	0.33	010	A:	3.64E-12	555	=k34
													Dog	2 2					
													קא	21 J					

Notes	=k36	=k37	=k25	=k26	=k24	=k27	=k27	=k27	=k27	=k27	=k27	2,4,5	2,4,5	=k122																									
$E_a/R^{(C)}$	500	500	500	500	500	500	500	500	500	510	510	510	510	510	510	510	300	300	300	300	300	300	300	500	500	500	500	500	500	500	0	0	0	0	0	0	0	855	855
$k_{298}^{(B)}$	1.87E-12	2.10E-12	1.51E-12	1.00E-11	1.20E-12	1.00E+04	1.00E+04	1.00E+04	1.00E+04	1.00E+04	1.00E+04	1.00E-12	7.40E-13	7.40E-13																									
										0.67 HO2																													
	80R2	80RO	70RO	60RO	50RO	40RO	30RO	20RO		.67 70RO +	.67 60RO +	.67 50RO +	.67 40RO +	.67 30RO +	.67 20RO +	.67 10RO +								НО	FCFO	FCFO	FCFO	FCFO	FCFO	FCFO									
	+	+	+	+	+	+	+	+		0 +								+	+	+	+	+	+	+	+	+	+	+	+	+									
cts	10RO	61CA	51CA	41CA	31CA	21CA	11CA	01CA	70RO	60RO	50RO	40RO	30RO	20RO	10RO	70RO	60RO	50RO	40RO	30RO	20RO	10RO	60R2	50R2	40R2	30R2	20R2	10R2	PROD	82R3	81R3								
Produ									2.00	0.33	0.33	0.33	0.33	0.33	0.33	0.33																							
	Ш	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	II	П								
(81R3	80R2	70R2	60R2	50R2	40R2	30R2	20R2	10R2	X02	NO	0N N	NO	0N N	0N N	0N N	0N N	HO2							10RO	НО	Ы												
ints ([#]	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+							+	+	+
Reacta	10R2	70R2	60R2	50R2	40R2	30R2	20R2	10R2	70R2	60R2	50R2	40R2	30R2	20R2	10R2	70R2	60R2	50R2	40R2	30R2	20R2	10R2	70RO	60RO	50RO	40RO	30RO	20RO	10RO	82CA	81CA								
	85	86	87	88	89	06	91	92	93	94	95	96	97	98	66	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123

 Table S5 Notes:
 A
 Chemical species names follow the key shown in Figure S1. XO2 is any organic peroxy radical (R₂C(H)-OO) and Page 13

is predominantly CH₃OO in the troposphere

- k₂₉₈ is the rate constant at 298 K and 1 atmosphere. Rate constants for unimolecular reactions have units s⁻¹ and for bimolecular reactions have units cm³ molecule⁻¹ s⁻¹ Б
 - C Temperature dependent rate constant $k_T = k_{298} \exp{-E_a(1/298 1/T)}$
- Rate constant set to the average of published measurements for this reaction; temperature dependence may be estimated as indicated by note 4
- 2 Rate constant data from IUPAC (2005)
 3 Pressure and temperature dependence de
 4 Rate constant estimated from data for sir
- Pressure and temperature dependence described by a Troe equation from IUPAC (2005)
- Rate constant estimated from data for similar compounds. Peroxy radical reaction rates are estimated from data for adical self-reactions and than rate constants for cross-reactions were set to the geometric mean of the self-reaction CH₃CH₂OO, CF₃CF₂OO, CF₃CHFOO, CH₃C(O)OO and CH₃OO. Rate constants were estimated for peroxy ates.
- where OH can hydrogen bond to the target (e.g., for alcohols and aldehydes) leading to negative activation energy Temperature dependence estimated. OH abstraction reactions were assigned positive activation energy except Smith and Ravishankara, 2002) S
- Product yields estimated by analogy with similar reactions and adjusted to match the product distributions observed n photo-reactor experiments 9
 - Rates of photolysis reactions depend upon solar irradiance (photons $\text{cm}^2 \text{ s}^{-1}$), absorption cross-section (cm^2) and quantum yield (photon⁻¹). Solar irradiances are calculated using the Tropospheric visible Ultra-Violet (TUV) model (Madronich, 2002)
- 82AL photolysis modeled with a quantum yield of 0.02 with absorption cross-sections for CF3CHO from Selleveg et al., (2004) ∞
- 81AL photolysis modeled with a quantum yield of 0.01 with absorption cross-sections for CF3CH2CHO from Selleveg et al., (2004) δ

Table S3 References

- IUPAC 2005. R. Atkinson, D.L. Baulch, R.A. Cox, J.N. Crowley, R.F. Hampson, R.G. Hynes, M.E. Jenkin, J.A. Kerr, M.J. Rossi, and J. Troe.
- 'Evaluated kinetic and photochemical data for atmospheric chemistry IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry." July 2005 web version available from http://www.iupac-kinetic.ch.cam.ac.uk/index.html
 - Madronich, S. (2002). "The Tropospheric Visible Ultra-Violet (TUV) Model.". Available from http://www.acd.ucar.edu/TUV/
- Sellveg, S.R., T. Kelly, H. Sidebottom and C.J. Nielsen (2004). A study of the IR and UV-Vis absorption cross-sections, photolysis and OH-initiated oxidation of CF3CHO and CF3CH2CHO. Physical Chemistry Chemical Physics, 6, (6), 1243-1252.
 - Smith, I.W.M. and A.R. Ravishankara (2002). "Role of Hydrogen-Bonded Intermediates in the Bimolecular Reactions of the Hydroxyl Radical" J. Phys. Chem. A, 106, 4798-4807



.

+0H / - H20 +02 / -H02

+HO2 / -03

♦

(PFNA) 81CA

+HO2 / -O2

81PA

+RO2 / -RCHO

810H

+HO2 / -O2

82PA

+HO2 / -O3

82CA



etc.

"Unzipping" Cycle

+RO2 / -RCHO

80OH

80AF

hydrolysis ŧ

ŧ

(PFOA) 71CA



Figure S3: Annual average ground-level air concentrations (pg m⁻³) of 8:2 FTOH from North American air emissions associated with the manufacture, use and disposal of DuPont fluorotelomer-based products.

- a) 8:2 FTOH with baseline (2004) release estimates
- b) 8:2 FTOH with future (2007) release estimates

The concentration ranges shown in these figures extend down to the concentration typically reported as the LOQ for detection of 8:2 FTOH in air (\sim 1-2 pg/m³).



Figure S4. Fractional yields of PFOA and PFNA from 8:2 FTOH in (a) February and (b) July of 2004.