HIGH RESOLUTION ATMOSPHERIC MODELING OF FLUOROTELOMER ALCOHOLS AND PERFLUOROCARBOXYLIC ACIDS IN THE NORTH AMERICAN TROPOSPHERE

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Introduction

Perfluorinated carboxylic acids (PFCAs) have been widely detected at low concentrations in multiple environmental systems, including water and air,[1,2] wildlife in the arctic[3] and human blood.[4-6] Though widely distributed, PFCAs are not expected to be transported over long distances in the atmosphere because they have high affinity for water and will be efficiently removed by both wet and dry deposition.[7,8] Atmospheric transport of compounds that can degrade to PFCAs in atmosphere (e.g., fluorotelomer and sulfonamide alcohols) has been proposed as a potential source of atmospheric PFCAs in the actic.[9,10] The fate and transport of FTOHs was recently investigated using a global-scale (4° latitude by 5° longitude grid) atmospheric model.[11] Our investigation uses a high-resolution atmospheric chemical transport model of North America to study relationships between air emissions of PFCAs and PFCA precursors associated with DuPont fluorotelomer-based products, atmospheric reactions and surface deposition of FTOHs and PFCAs. A detailed chemical mechanism of atmospheric FTOH degradation was developed and tested against the chamber study of Ellis *et al.*[9] This mechanism was incorporated into a photochemical grid model covering continental North America with 72-km grid and hourly temporal resolution to explicitly model direct transport and surface deposition of PFCAs and PFCA precursors within North America and to the North American Arctic. The modeling effort identifies intermediate compounds that are important to the formation of PFCAs from the degradation of FTOHs. This work also identifies the fraction of FTOH that react to form PFCAs within the continental "airshed" and the fraction that exits to the global troposphere.

Modeling Approach

A detailed mechanism involving 123 reactions and 41 chemical species was developed to describe the gas-phase atmospheric degradation of 8:2 FTOH, a residual raw material in fluorotelomer-based products, to intermediate and final products as small single carbon species (e.g., CO, CF_2O). The mechanism follows the scheme outlined by Ellis *et al.*,[9] with some significant differences. For example, our proposed mechanism includes CO elimination from the perfluoroalkoxy radical. Rate constants and product distributions for individual reactions were based on published data for each reaction where possible or by analogy with similar compounds.[12]

The degradation of the hydrocarbon portion of 8:2 FTOH can proceed via OH radical and photolysis reactions. PFNA can be formed by reaction of a perfluorinated peroxyacyl radical with HO_2 radical. PFOA can be formed via reaction of a perfluorinated peroxy radical with an RO_2 radical (e.g., CH_3O_2). 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.[12] 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 CF_2O and potentially smaller PFCAs (perfluoroheptanoic acid – PFHpA, perfluorohexanoic acid – PFHxA, etc.) by reactions analogous to those that form PFOA.

The developed chemical mechanism predicts that atmospheric yields of PFCAs from FTOHs depend upon the abundance of NO and therefore atmospheric modeling should be capable of distinguishing "high NOx" from "low NOx" regions. High NOx regions of the atmosphere are closely associated with major anthropogenic sources of NO emissions such as urban areas and major point sources 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.[13] The latest 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 3-D 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, SO_2, NH_3 and aerosols were from 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.[14]

In the model, prevailing westerly winds over the continent transported some FTOH releases out of the eastern boundary of the CAMx modeling domain before they had completely reacted. The fraction of FTOH emissions exiting the domain varies by season according to wind patterns, oxidant levels and where the FTOH emissions occur. FTOH and degradation products could be transported out of the domain, continue to react while circling the globe, and then return to the domain to react further and/or deposit. To model this recirculation, FTOH and products that exited through the eastern domain boundary were allowed to continue to react and deposit in a global domain, approximated by a box model. The FTOH and products were assumed to react for 30 days in the global box model and to encounter a precipitation event every five days.[15] Unreacted FTOH and products from the box model were then re-introduced along the western and northern domain boundaries.

Air emissions simulated with the model were estimated for PFCAs and FTOHs associated with the production, use, and disposal of DuPont's fluorotelomer-based products in North America. Manufacturing emissions were located geographically while use and disposal emissions were located based on population density. Two release time frames were modeled, a baseline case with releases based on 2004 production and sales data and 2004 residual profiles and a future case based on 2004 production and sales data with 2007 residual profiles. Longer chain FTOHs (i.e., 10:2, 12:2 and 14:2 FTOH) were included in the model by assuming the same reaction yields developed for 8:2 FTOH.

Results and Discussion

The chemical mechanism developed for 8:2 FTOH was tested against the chamber experiment reported by Ellis *et al.*[9] Chemical degradation of FTOH in the chamber was initiated by Cl-atoms rather than OH radicals and so Cl-atom reactions were added to the mechanism. The chamber experiment was performed without added NO emphasizing the role of peroxy radical reactions that lead to PFCA production. The measured PFCA yields after 94% destruction of 8:2 FTOH were 1.6%, 1.5%, 0.32%, 0.24% and 0.1% for PFNA, PFOA, PFHpA, PFHxA and PFPA (perfluoropentanoic acid).[9] Our chemical mechanism predicts PFCA yields of 1.1%, 0.9%, 0.71%, 0.57% and 0.44% for PFNA, PFOA, PFHpA, PFHxA and PFPA under the conditions of Ellis *et al.*[9] The agreement between our modeled PFCA yields and the reported yields is reasonable and supports use of our mechanism for atmospheric modeling.

Modeled PFOA concentrations for the North American domain reflect direct PFOA (present as an unintended reaction by-product in fluorotelomer-based products) emissions and secondary PFOA formation from 8:2 FTOH, whereas PFNA concentrations reflect only secondary formation from 8:2 FTOH. Global recirculation of FTOH and its degradation products outside the CAMx domain are included. For the baseline scenario, 25% of the released 8:2 FTOH reacted before exiting the CAMx domain and the resulting yields of PFOA and PFNA within the CAMx domain were 0.58% and 0.41% of the 8:2 FTOH reacted. Allowing the unreacted FTOH and its degradation products to react outside and then reenter the CAMx domain (i.e., global recirculation, discussed above) raised the yields of PFOA and PFNA within the CAMx domain to 0.84% and 0.44%, respectively, and raised the total fraction of 8:2 FTOH consumed to 66%. PFCAs formed by reactions outside the CAMx domain were mostly removed by wet deposition before they reentered the CAMx domain. The higher yields of PFOA and PFNA within the CAMx domain with recirculation included are attributable to FTOH degradation products (principally the aldehydes 82AL and 81AL) forming outside the CAMx domain, reentering the CAMx domain, and then reacting to form PFCAs. Understanding the fate of these fluorinated aldehydes in the atmosphere is important to understanding the relationship between FTOH emissions and PFCA deposition because the fluorinated aldehydes are significant reservoir species. When air concentrations were scaled to account for the contribution from the FTOHs with chain lengths longer than the 8:2 FTOH, the longer FTOHs contributed approximately 34% of the total PFOA formed from atmospheric reaction. Similarly, approximately 51% of the total PFNA formed from atmospheric reactions results from FTOHs with chain lengths greater than the 8:2 FTOH.

Overall, the predicted atmospheric inputs of PFOA and PFNA from fluorotelomer-based products to the North American modeling domain are extremely low, 160 kg/yr of PFOA and 50 kg/yr of PFNA. These values are significantly lower than estimated direct PFCA environmental releases reported previously.[16] Comparison of the baseline and future modeling results indicates that atmospheric inputs of PFCAs in North America are predicted to decline by an additional order of magnitude as a result of planned industry process improvements which will reduce manufacturing emissions and lower the residual fluorotelomer raw material and trace PFCA content of fluorotelomer-based products.

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CANADIAN ECOLOGICAL RISK ASSESSMENT ACTIVITIES ON PFOS, PFOA AND OTHER PERFLUORINATED SUBSTANCES: CONSIDERATIONS FOR THE DETERMINATION OF BIOACCUMULATION POTENTIAL

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Introduction

Perfluoroalkyl substances are persistent and ubiquitous chemicals that are used in a variety of products and applications such as polymers, stain repellents, lubricants, paper coatings and cosmetics[1]. The widespread and global occurrence of perfluoroalykyl substances in various media (biota, water, sediment, air and dust) has been noted by many researchers [2-9] Their ubiquitous presence in the environment combined with their persistence, their tendency to accumulate in certain tissues, and their toxicity have made this class of substances a priority for international risk assessments. In Canada, the ecological risk assessment of perfluorooctane sulfonate (PFOS), its salts, and its precursors, is close to being completed. The assessment finds PFOS to be bioaccumulative, persistent and toxic. The bioaccumulation criteria used for categorization in Canada was developed for lipid-partitioning organic substances. This presents a challenge for assessing substances which bioaccumulate though different mechanisms such as perfluorinated substances, which preferentially bind to proteins. An ecological review of perfluorooctanoic acid (PFOA) and its salts is also underway. In the context of Environment Canada's categorization exercise under the *Canadian Environmental Protection Act, 1999* (CEPA 1999), preliminary findings for additional perfluorinated substances on Canada's Domestic Substances List (DSL) are reported. The priorities for conducting future assessments on perfluorinated substances will be partially based upon these categorization findings.

Methods

Under CEPA 1999, an assessment of a substance is conducted to determine whether "...a substance is toxic or if it is entering or may enter the environment in a quantity or concentration or under conditions that: (a) have or may have an immediate or long-term harmful effect on the environment or its biological diversity; (b) constitute or may constitute a danger to the environment on which life depends; or (c) constitute or may constitute a danger in Canada to human life or health." [10]

The ecological risk assessments are generally carried out according to guidance and existing criteria for bioaccumulation and persistence for existing substances. The Government of Canada's *Persistence and Bioaccumulation Regulations* under CEPA 1999[11] (see Table 1) are based on the Toxic Substances Management Policy (TSMP) persistence and bioaccumulation criteria[12] which were first developed in the mid 1990's and formally published in 1995. The Existing Substances Division (ESD) of Environment Canada considered the comments received during the 60-day public comment period (October-December 2004) and revised the PFOS assessment, as appropriate.

Table 1. Persistence and Bioaccumulation Criteria of the *Canadian Environmental Protection Act, 1999* Regulations[11]

Persistence		**Bioaccumulation**
Medium	*Half-life*	
Water	>= 6 months	BAF >= 5000 or
Sediment	>= I year	BCF >= 5000 or
Soil	>= 6 months	log Kow >= 5.0
Air	>= 2 days	
Evidence of Long Range Transport (atmospheric)		