

Throughout this document, reviewer comments are in black and author responses are in blue.

Reviewer 1:

Summary comments: The title and abstract of the paper were highly promising.
We have edited the title and abstract to be more precise about the details of our study.

The title has been changed from “Uncertainty and variability in atmospheric formation of PFCAs” to “Uncertainty and variability in atmospheric formation of PFCAs from fluorotelomer precursors”

We have added the following sentence to the first paragraph of the abstract: “In particular, we examine the variability in PFCA formation in different chemical environments, and estimate the uncertainty in PFCA formation due to reaction rate constants.” Line 10 (ca. Line 10 of the original manuscript)

In my opinion, however, the paper makes only a small contribution to scientific progress in this field. The authors model the formation of PFOA and PFNA from 8:2 FTOH, which has been done several times before.

While the reviewer is correct that the formation of PFOA and PFNA from FTOH has been modeled before, we believe our knowledge of these processes can be improved by further modeling. Here, we focus on quantifying the variability in PFOA and PFNA formation in different photochemical environments and estimating the uncertainty in PFOA and PFNA formation due to the rate constants of the reaction mechanism. Neither of these goals has been addressed by previous efforts.

In order to make this clearer, we have changed the abstract to be more precise:
we have added the word “fluorotelomer” to the lines

“We evaluate PFCA formation with the most complete degradation mechanism to date to our knowledge, using a box model analysis to simulate the atmospheric chemical fate of *fluorotelomer* precursors to long-chain PFCAs.” Line 6
and

“We calculate long-chain PFCA formation theoretical maximum yields for the degradation of *fluorotelomer* precursor species at a representative sample of atmospheric conditions from a three dimensional chemical transport model...” L9

We have also added the following sentence to the introduction: “Our goal in this work is to examine the variability in PFCA formation in different chemical environments, and estimate the uncertainty in PFCA formation due to reaction rate constants.” L66

The authors claim that they have used “...the most complete degradation mechanism to date...”.

It appears that the photochemical environments and environmental conditions are very well described. However, the authors miss many important precursors of PFOA, including perfluorooctane sulfon-amides (FOSAs), perfluorooctane sulfonamidoethanols (FOSEs), 10:2 FTOH etc. and miss to discuss these uncertainties in the discussion.

We focus our analysis on 8:2 fluorotelomer precursors, but do not mean to discount other precursors. We have added discussion of how our results apply to fluorotelomer precursors of lengths 10:2 etc. (see below), and have added the following discussion of other precursors, along with further points addressed separately below:

“We quantify the theoretical maximum yields of formation of lC-PFCAs from fluorotelomer precursor, but there are other precursors that follow different degradation schemes and would therefore yield PFCAs in different quantities for the same environment. Precursors such as FOSAs and FOSEs are found along with FTOHs in the remote atmosphere (Shoeib et al. 2006) and are also precursors to PFOS. Some fluorotelomer precursors such as fluorotelomer olefins follow only a subsection of our reaction mechanism because of their structure, and would have higher theoretical maximum yields.” L326

They also miss to discuss the possibilities of direct transport of APFOA (the ammonium salt of PFOA) from polytetrafluoroethylene (PTFE) manufacturing and marine (sea spray) aerosol transport of PFCAs. Even if the authors do not think these processes are important they deserve discussion.

While the direct emission and transport of PFOA and its salts is important, it is not the focus of this study. To better put this study into context, we have added discussion in response to the reviewer's specific comments below, as well as adding to the introductory paragraph the sentence:

“PFCAs and their salts are directly emitted to the environment and can be transported long distances via the ocean, having important consequences for remote aquatic biota.” L31

There are atmospheric measurements of FTOH in air from various locations and measurements of PFCAs in precipitation also from various locations. Why were these not discussed or used as a basis for model evaluation?

As we discuss in response to comments by Reviewer 2, our calculations of the capacity of different photochemical environments to form PFCAs are not simulations of actual yields of PFCAs at these points, and it would be difficult to infer from our calculations what the concentrations of precursor and PFCAs would be at the location and time of measurements. This kind of comparison is better suited for a model which accounts for emissions, transport, and non-chemical fate of PFCAs, their precursors, and intermediate compounds.

Overall I was very disappointed with the weak discussion; i.e. failure to put the work into proper context.

We hope that after our changes to address the reviewer's specific comments and those of the other reviewer, the discussion has better put this work into context for the reader.

In addition to the changes in response to the reviewer's specific comments below, we have also

added the paragraph:

“The uncertainty and variability estimates that we present indicate quantitatively that the most important piece of information for calculating atmospherically formed PFCAs is their photochemical environment, and that explicitly accounting for transport in the atmosphere on top of chemistry would give accurate estimates of yielded PFCAs despite uncertainty in the rates of the chemistry involved. This means that the approach of previous studies that use spatially resolved models (Wallington et al., 2006; Yarwood et al., 2007) is one the most important to our understanding of atmospherically generated PFCAs and should be continued in the future. Our results also show, however, that accounting only for regional-scale transport as in Yarwood et al. (2007) could miss an important fraction of the atmospherically formed long-chain PFCAs, since the capacity for remote atmospheric conditions to form them is so high. Continued quantitative study of the chemistry of atmospheric PFCA formation, through updating the chemical mechanism, by accounting for the changes in the photochemical environment brought on by synoptic variability, and accounting for anthropogenic emissions changes relevant to both HOx-NOx photochemistry and PFCAs themselves has further value over the previous work.” L326

And in response to the other reviewer we have added the following changes relevant to this discussion:

We have added the following discussion (to put our environment categorization into the context of transport through these different environments) and figure after the sentence “Depending on how long precursor and intermediate species reside in the different atmospheric regions and the distribution of emissions, yields of lcPFCAs can vary greatly.”:

“To illustrate this point, figure 5 shows the time series of the fate of a unit of fluorotelomer precursor released from the eastern U.S. and following a trajectory calculated by the HYSPLIT dispersion model, through our photochemical environments. Starting in a relatively high NOx environment, the precursor is quickly reacted and short-chain compounds form quickly at the beginning. As the parcel of air is transported over the Atlantic Ocean and poleward, long chain PFCAs begin to form more quickly. The remaining intermediates at the end of this period have the potential to form much more PFOA and PFNA depending on the future fate of the air parcel. Despite emission into a very low-maximum yield environment, the transport is sufficiently fast to allow long-chain PFCA formation.” L326

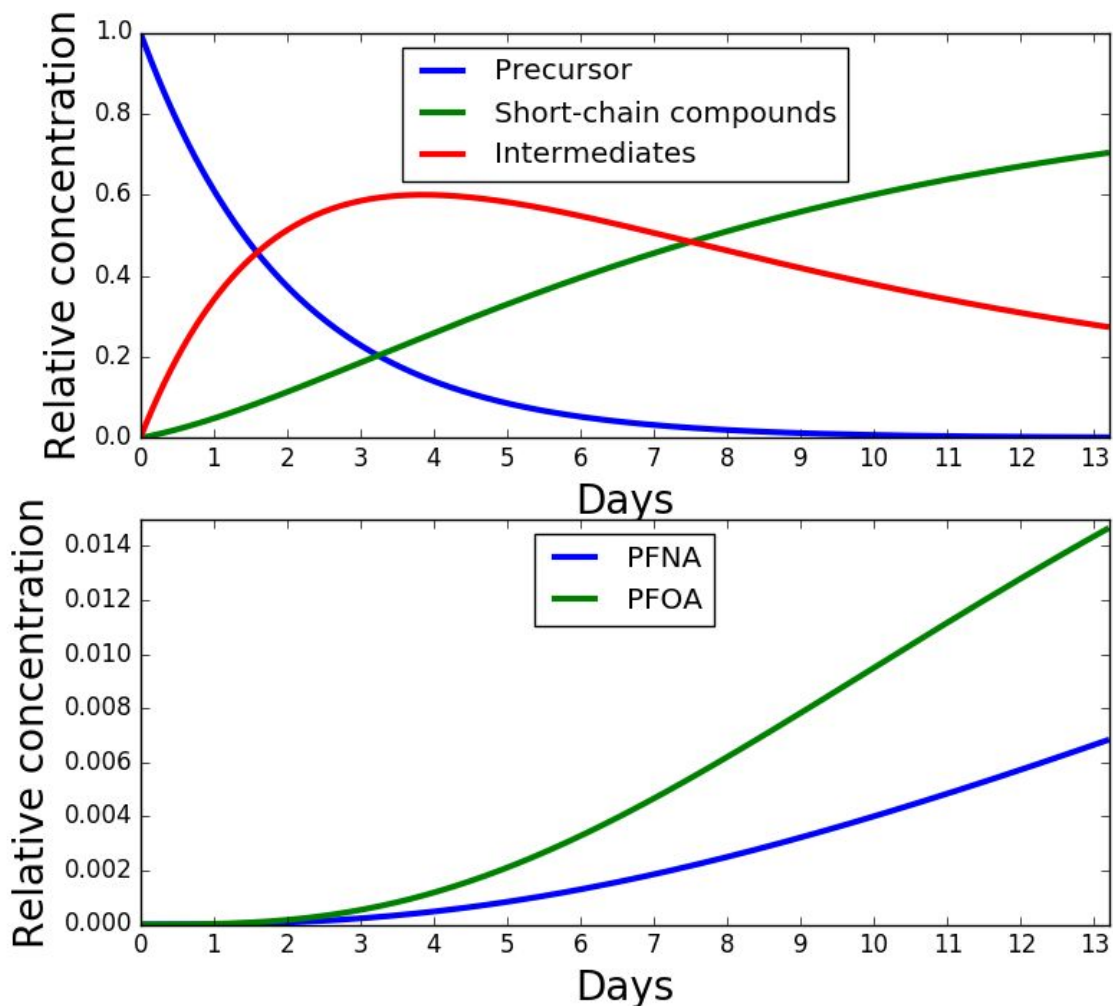


Figure 5. Fluorotelomer precursor chemical fate along HYSPLIT trajectory through summertime photochemical environments. After two weeks, yields of PFOA and PFNA are approximately 1.5% and 0.7%, respectively, with more than 20% of the initial precursor still in an intermediate form which will undergo further reactions.

After reading the manuscript I'm not any wiser with regard to the importance of FTOH degradation compared to other sources of PFCAs to the global environment. If there are other similarly negative reviews then the editors may want to consider rejection. We acknowledge the reviewer's point – however, the goal of this paper is not to quantify the importance of FTOH degradation compared to other PFCA sources to the global environment. We hope that our revised abstract and introduction help the reader to better understand the paper's goals.

Specifically, we highlight with this paper the importance of environment for the atmospheric formation of PFCAs and to estimate the uncertainty involved in the chemical mechanism, which has not been done in prior works to our knowledge. While we do not make statements about the importance of fluorotelomer precursors vs. other PFCA precursors, we hope that readers of this study would be wiser with regard to the degradation of fluorotelomer compounds in the atmosphere. To highlight the importance of uncertainty and variability themselves, we have added to the end of the first Discussion paragraph:

“The greater impact of variability compared to uncertainty means that it is quantitatively viable to model the transport and chemical fate of emissions despite a relatively uncertain set of chemical reactions.” L196

Specific comments:

Line 25: perfluoroalkyl carboxylic acids is now the preferred name.

We have changed all instances to perfluoroalkyl carboxylic acids

Line 28: no year given in Scott et al.

We have added 2006 to the reference.

Line 29: Define precisely what you mean by "long-chain PFCAs"

We have added the parenthetical “(PFCAs of chain length greater than 7)”

Line 30: rephrase "increased detrimental effects". I presume the authors mean bioaccumulation potential or toxicity or both?

We have changed “increase of detrimental effects” to read “increased bioaccumulation”

Lines 44-50: Authors miss to discuss other important precursors (see above).

We have changed the sentence “However, studies have indicated that other emitted atmospheric precursors exist in the form of other fluorotelomer compounds.” to read “However, studies have indicated that other emitted atmospheric precursors exist in the form of other fluorotelomer compounds, perfluoroalkyl sulfonamides (FOSAs), and perfluoroalkyl sulfonamidoethanols (FOSEs).” L45

We have also added discussion of those species that are not the focus of this work, below.

Lines 78-84: Are all chemical species assumed to be in the gas phase throughout the reactions?

What are the uncertainties generated by this assumption? For example, can reaction intermediates not sorb to aerosols or be rained out?

Yes, in our model the chemical species are in the gas phase. Removal through non-reaction processes such as sorption and rainout would dampen the yields compared to our calculations (if precursor or intermediate) or not affect them (if PFCA end products). For this reason, we call the result of our calculations “maximum theoretical yields”. To clarify our model, we have made the following changes:

We have added “gas-phase” to the sentence “We use a box model representation of the *gas-phase* chemical reactions that lead to atmospheric PFCA formation to calculate yields per unit precursor species.” L78

and have extended the sentence

“To quantify an upper limit of possible atmospheric PFCA formation, we calculate yields of PFOA and PFNA in the absence of non-chemical loss processes.” to read

“To quantify an upper limit of possible atmospheric PFCA formation, we calculate yields of PFOA and PFNA in the absence of non-chemical loss processes, such as sorption to atmospheric particulate matter or removal by wet or dry deposition.”.L81

Line 95: "Shorter chain substances" are also generated but it is not specified which or what their yields and formation times are. Why not? This is also highly interesting.

Given the assumption of no non-chemical removal processes and making the assumption that the relative rates at branching points are independent of chain length, our calculations can be extended analytically to apply for longer or shorter chain precursors and products. We have therefore added the following text and table to the discussion section:

“In the future, if production does shift to shorter chain fluorotelomer products, our findings will apply to correspondingly shorter chain PFCAs formed in the atmosphere, as the chemistry studied is analogous across the homologue series. With the assumption that relative rates at the branching points do not depend on chain length, our calculations can be extended to longer and shorter precursor homologues and correspondingly longer and shorter product homologues. If $Y(9)$ and $Y(8)$ are our calculated maximum yields for PFNA and PFOA, respectively, then the fraction f_{PFCA} of PFCA formation from the “unzipping” step of the mechanism is

$$f_{PFCA} = Y(8)/(1 - Y(9)) .$$

Knowing this fraction, yield calculations can be extended to shorter and shorter chain PFCA products using the formula

$$Y(X) = f_{PFCA} \left(1 - \sum_{i=x+1}^{longer} Y(i) \right)$$

where the theoretical maximum yield at a given product chain length can be calculated based on the yields of the longer chain products in a given environment.

As an example, the table below shows the extension of the Arctic case where the theoretical maximum yields of PFNA and PFOA are 18% and 20%, respectively.” L335

Table:

| Product | 12:2 precursor | 10:2 precursor | 8:2 precursor | 6:2 precursor |
|---------|----------------|----------------|---------------|---------------|
| PFTrDA | 0.18 | 0.00 | 0.00 | 0.00 |
| PFDODA | 0.20 | 0.00 | 0.00 | 0.00 |

| | | | | |
|-----------|------|------|------|------|
| PUnDA | 0.15 | 0.18 | 0.00 | 0.00 |
| PFDA | 0.11 | 0.20 | 0.00 | 0.00 |
| PFNA | 0.09 | 0.15 | 0.18 | 0.00 |
| PFOA | 0.07 | 0.11 | 0.20 | 0.00 |
| PFHeA | 0.05 | 0.09 | 0.15 | 0.18 |
| PFHxA | 0.04 | 0.07 | 0.11 | 0.20 |
| PFPeA | 0.03 | 0.05 | 0.09 | 0.15 |
| PFBA | 0.02 | 0.04 | 0.07 | 0.11 |
| PFPrA | 0.02 | 0.03 | 0.05 | 0.09 |
| TFA | 0.01 | 0.02 | 0.04 | 0.07 |
| Remainder | 0.04 | 0.07 | 0.12 | 0.20 |

Lines 200-215: It is very hard to follow the reaction scheme; an overview figure would have been useful here.

We have added a diagram of the reaction scheme, and corresponding reaction numbers to the Appendix.

Lines 170-230: It would be useful

to point exactly what is the novel contribution in the results. What does this study add to previous studies by e.g. Yarwood et al. 2007 nearly a decade ago? They already showed how NO_x in populated urban affects PFOA yields.

To put our contribution into clearer context, we have added/changed the following:

“Previous work (Yarwood et al., 2007) quantified yields of PFOA and PFNA over the United States, but the extreme capacities to yield lCPFCAs in remote low-NO_x environments have been previously unquantified.” Line 187

“For both species, yields are negligible under the high-NO_x urban conditions, in agreement with previous work focused on North America (Yarwood et al. 2007).” Line 190

“In summary, we determine for the first time the dominant sources of uncertainties in theoretical maximum yields of PFOA and PFNA, finding that rate constants of reactions of NO and RO₂ with poly- and per-fluorinated peroxy radicals are the leading sources in the degradation chemistry.” Line 217

“Figure 3(b) shows that the same clusters also correspond to Arctic and lower-latitude environments, respectively, indicating a distinct photochemical environment for PFCA formation in the Arctic atmosphere that to our knowledge has not been discussed in previous studies.”

Line 226

Line 241-242: Explain what you mean by "different conditions within the Arctic"?

To clarify, we have changed the sentence "The former shows relatively constant theoretical maximum yields across different conditions within the Arctic, with a large range of formation times that are independent of the yields." to read

"The former shows relatively constant theoretical maximum yields across *all of the conditions within* the Arctic, with a large range of formation times that are independent of the yields" L241

Lines 300-345. The final discussion excludes many important atmospheric processes including direct atmospheric

transport of PFOA following release from manufacturing and marine aerosol transport.

The authors also fail to consider atmospheric and deposition measurements of FTOHs and PFCAs. I'm presuming that the model was not able to calculate precipitation scavenging so that comparisons could be made with PFCAs measured in precipitation?

To the end of the discussion section we have added the following:

"We quantify variability in atmospherically formed PFCAs but direct emissions and transport of PFOA and its salts are also environmentally relevant, as transport to remote regions through the ocean has historically likely been dominated by these direct emissions (Wania 2007)." L345

And to the end of the conclusion sentence we have clarified the final sentence to read:

"While the atmosphere is a potentially growing source of lCPFCA in the Arctic, oceanic transport of directly emitted, and to a lesser extent low-latitude atmospherically generated, PFCAs are likely more important pathways to the Arctic for lCPFCA." L365

Several precursors of PFOA are missing (see above). Note there is evidence that 10:2 FTOH can also form PFOA (see Myers and Mabury (2010) Environmental Toxicology and Chemistry, Vol. 29, No. 8, pp. 1689-1695). Also it is well known that perfluorooctanesulfonyl fluoride (POSF)-based precursors can form PFCAs and levels of these POSF-based precursors (e.g. FOSEs) have not declined since the 3M phase-out.

We believe that we have addressed these concerns in the responses above.