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 lCPFCAs 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
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

\[
f_{PFCA} = \frac{Y(8)}{1 - Y(9)} .
\]

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

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

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:

<table>
<thead>
<tr>
<th>Product</th>
<th>12:2 precursor</th>
<th>10:2 precursor</th>
<th>8:2 precursor</th>
<th>6:2 precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFTrDA</td>
<td>0.18</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>PFDoDA</td>
<td>0.20</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
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 NOx 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-NOx environments have been previously unquantified." Line 187

“For both species, yields are negligible under the high-NOx 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 perfluoroocotanesulfonyl 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.
Reviewer 2:

Summary of manuscript
The authors investigate, using a chemistry model, the theoretical maximum yield of formation of select long chain perfluorocarboxylic acids (perfluorooctanoic acid, PFOA, and perfluorononanoic acid, PFNA) from precursor species (fluorotelomers). PFOA and PFNA are persistent organic pollutants which bio-accumulate and have detrimental biological effects. The authors use an updated chemical mechanism in a simplified modeling approach (box model vs. spatially resolved atmospheric chemistry model), relative to previous modeling works (Wallington et al., 2006, Yarwood et al., 2007). In the simulations, some loss terms (wet and dry removal) are ignored, hence yields of formation of PFOA and PFNA are theoretical maxima. The authors conduct an interesting analysis of uncertainty propagation which identifies the rate coefficients that have the largest contribution to the uncertainty in the yields of formation of PFOA and PFNA. Central results of the study are that less than 10% of emitted fluorotelomer precursors yield PFCAs, and that atmospheric conditions farther from pollution sources (low NOx environments) have both higher capacities to form long chain PFCAs and higher uncertainties in those capacities. With the calculated median theoretical maximum yield from their simulations and a current estimate of global precursor species emissions, the authors estimate the atmospheric production of long chain PFCAs at 50 t/yr.

We thank the reviewer for their thorough reading of our manuscript and their comments below.

The manuscript has merits, some avoidable oversight errors, and a critical flaw. The merits include the interesting and useful analysis of uncertainty propagation which identifies the rate coefficients that have the greatest contribution to uncertainty in the yield of formation of the species of interest. Such analysis is useful for laboratory experiments, which can in turn reduce uncertainty of simulations. The analysis of the chemical flux through the reaction mechanism in different environments is instructive and helps increase understanding of the conversion of fluorotelomers to PFCAs. The manuscript is well written, its language is clear and concise.

The critical flaw is the use of a box model. The chemistry simulations are conducted with fixed chemical conditions ("The single-box model simulates the chemical reactions discussed above, treating the concentrations of HOx, NOx, Cl, and RO2 as constant ... until all of the initial precursor has reached one of the reaction end-points (PFNA, PFOA, or shorter-chain PFCAs).".). This neglects changes in chemical conditions that air parcels experience as they are transported. A box model is appropriate to investigate chemical processes which proceed on time scales that are much shorter than transport time scales. A good example is OH chemistry and certain other chemical processes with time scales that are typically shorter than a diurnal cycle. In the present work, the authors investigate the conversion of fluorotelomers via fluorotelomer aldehydes (FTAL) to PFOA and PFNA. The chemical
scheme in the simulations sets out from FTAL (under the assumption that FTAL forms quickly from the precursor fluorotelomers). FTALs are converted in reactions with OH and Cl (and by photodissociation) to perfluoroacyl peroxy radicals (followed by subsequent transformation towards PFOA and PFNA). The OH and Cl reactions are fairly slow: With the reaction rate coefficients given by the authors and assuming \([\text{OH}] = 1E6 \text{ cm}^{-3}, [\text{Cl}] = 1E5 \text{ cm}^{-3}\), the corresponding time scales are 5.8 days and 6.1 days, respectively. Transport and mixing are bound to occur on these time scales (the issue is compounded by the very long time of formation of PFOA and PFNA identified the simulations, which exceeds 50 days). The investigation of yields of formation of PFOA and PFNA, a key focus of the present work, makes hence little sense given that air parcels are likely to move away from a location with a specific chemical regime to another on the time scales of the chemistry.

We agree that the rate of formation of PFCAs will be much longer than the residence times of given air masses in any one particular environment. We do not wish to convince the reader that the yields we calculate are useful because we believe that the species will sit at these conditions until the precursors become end products, but rather we highlight in a quantitative way the differences in conditions for PFCA formation that the species involved can experience in the atmosphere. Theoretical maximum yields here are a way to quantify the PFCA production capacity of that atmospheric environment, and not intended to match the fate of a single air parcel. We agree that the actual yield per precursor will be determined by mixing and transport likely across many of these environments due to the timescales mentioned, but believe that there is value in quantifying the differences between such environments. In particular, we have made changes to the abstract, introduction, and discussion (in response to Reviewer 1) to better communicate the goals of our analysis:

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)

We have 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

... 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

The product yields calculated with the chosen approach would reflect reality if air parcels would remain in a given chemical environment longer than the chemical formation of the product, but this seems unlikely. We agree that the theoretical maxima for yields that we calculate do not reflect the reality for any given parcel of air, for the reasons that the reviewer describes. The
Theoretical maximum yield here is a quantification of a given set of conditions’ capacity for forming PFCAs. We write “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.”

The issue extends to the analysis of uncertainty propagation from chemistry rate coefficients to product yields. This is the other key focus of the manuscript and one of its interesting parts. In it, the authors determine that it is the reactions of NO and organic peroxy radicals with poly- and perfluorinated peroxy radicals that dominate uncertainty in theoretical maximum yield of PFOA and PFNA. The information is useful for laboratory studies. The identified overall uncertainties are small - theoretical maximum PFOA and PFNA yield ranges (presumably 1-sigma) of 17-22 % and 78-85 % are found. However, given the long formation times from the precursor species to PFOA and PFNA, transport and mixing should be expected to matter - air parcels containing precursor species will experience different conditions on the product formation time scale. The actual product yield may differ from the yield calculated in fixed conditions with a box model. The product yields calculated in the present work hence contain uncertainty introduced by the box model approach.

We agree that if used predictively as actual yields, our calculated theoretical maximum yields will overestimate and hence contain uncertainty that is greater than that from the rate constants. (See above)

How does this uncertainty compare with the fairly small uncertainty arising from uncertainty in the rate coefficients? We agree that this is an important point, and as discussed above have added the sentence “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

Consider that on the formation time scale of PFOA and PFNA (weeks), an air parcel can experience very different chemical conditions, from highly polluted to oceanic or Arctic. This consideration casts doubt on one of the conclusions of the manuscript, "The greatest uncertainty reductions can be achieved by better quantifying rate constants at the branching points of the degradation chemistry."

To be more precise and reflect our meaning here, we have changed this sentence to read “The greatest uncertainty reductions through reaction rate determinations can be achieved by better quantifying rate constants at the branching points of the degradation chemistry.” L351

A more interactive model approach, in which transport and mixing and the associated change in physical and chemical conditions are accounted for could reduce uncertainty to a greater degree than reducing uncertainty in the rate coefficients.

We agree that a model approach that accounts for mixing and transport and changes in physical
and chemical conditions is important for simulating or predicting the specific fate of given real-world emissions, but do not consider this a reduction of uncertainty, per se, in our context. To make this more clear, we have changed the term “uncertainty” to “parametric uncertainty” in places that it was ambiguous.

A more interactive model approach (which avoids running a full-fledged atmospheric model) would be to run the chemistry box model along trajectories. Trajectories can be obtained from spatially resolved models using trajectory models such as HYSPLIT or FLEXTRA. It may be possible in this way to extract physical and chemical properties along trajectories from the GEOS-Chem model used by the authors.

We think that this would be an excellent way to illustrate the interactions of the different photochemical environments over the lifetime of an air parcel containing precursor species, and have added an example of this to our discussion.

We have added the following discussion 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.”
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.

This approach is more complex than a box-model approach and poses difficulties of its own, but has advantages: Back-trajectories from select deposition regions (such as the Arctic) can be identified and traced back to source regions. The chemistry box model can then be operated with chemical and photochemical input from GEOS-Chem along the trajectories (thereby accounting for change in chemical composition along the trajectories). Thus, one can, in principle, calculate the overall yields on trajectories leading from select emission regions to select deposition regions. The transport issue would be mitigated (although mixing and non-chemical removal would still not be accounted for) and yield attribution to individual sources would become possible.

We do believe that a detailed version of this would be an interesting study to perform, but also
believe that it is outside the scope of this study. We have added an illustrative version of this concept, as described above.

The manuscript contains a critical flaw: A box model with fixed chemical conditions is used to investigate chemical processes that take place on time scales during which chemical conditions are bound to change due to transport and mixing. I recommend a major revision only if the authors can compellingly demonstrate that the box model approach with fixed conditions is appropriate to investigate formation of PF-CAs from fluorotelomers, despite the formation taking place on time scales during which air parcels are transported and experience different chemical conditions. We acknowledge that PFCA formation timescales are longer than the residence times in any given chemical environment, but would argue that it is informative to know the differences due to the environment themselves, particularly in how those differences compare to the uncertainty due to the reaction mechanism, as the reviewer points out above.

One way to demonstrate this would be to show that systematically using fixed chemical conditions gives, in reasonable approximation, the results one would obtain if realistic, changing conditions were used. We do not believe that this would be the case, for the reasons that the reviewer points out in the above comments.

If this is not possible I recommend rejection in favor of a re-submission in which a more appropriate modeling approach, such as the outlined trajectory approach, is implemented.

Some detailed comments

For the benefit of the reader and to facilitate reproducibility, the below comments should be addressed and oversight errors corrected.

Section 2.1
- The numerical solver of the chemistry model should be briefly described.
  We have added the sentence "We use the LSODE solver implemented in the scipy package of Python to solve the system of differential equations defined by this chemistry." L84

Section 2.2
- Diurnal cycle: Is it resolved in the simulations, or does the model use perpetual mean conditions, without diurnal cycle variation? Simulations resolving the diurnal cycle would be preferable, being more realistic, but if the latter approach was chosen: how were daily mean photochemistry rates calculated? Was the perpetual mean conditions approach tested by select simulations that do resolve the diurnal cycle, and what were the results? Such a test is inexpensive when a box or a trajectory model is
We used the perpetual conditions after testing with a diurnal cycle. The reason that mean conditions provided such a similar response is that a) the chemistry involved scales with time of day fairly uniformly, meaning that competing processes tend to speed up and slow down together; b) there are no non-chemical processes in our model competing with these processes that scale together; c) there are no reactions in our mechanism or in the literature to our knowledge which would be dominant during the nighttime.

- Actinic flux specification: A value of 1E15 photons cm-3 s-1 at 90 degrees solar zenith angle is given (with reference to Seinfeld and Pandis, 2006). There are several issues which should be addressed: The units of actinic flux are photons cm-2 s-1, not photons cm-3 s-1. Solar zenith angle is measured from zenith: 90 degrees means the sun is at the horizon. This is inconsistent with the specification "peak actinic flux", which, in clear-sky conditions, occurs at noon (corresponding to a solar zenith angle that is typically >= 0 but < 90).

Thank you for pointing out these two typos, we have changed 90 degrees to 0 degrees and cm-3 to cm-2. L114

Seinfeld and Pandis (2006, Table 4.3) give 340-365 nm mean winter (5E14 cm-2 s-1) and summer (8.9E14 cm-2 s-1) noon actinic flux values at the surface, at 40 degrees north. The actinic flux value used in the simulations is only consistent with the summer value given in Seinfeld and Pandis (2006). The peak values here are scaled by latitude and time of year to translate this peak flux for all the photochemical environments. We have changed the sentence to read "Available photons for photolysis reactions were calculated based on a scaling by the position of the sun as a function of latitude and time of year and an assumption of clear sky conditions (Russell), and a peak actinic flux of 1x10^15 photons cm−2 s−1 at 0 degrees solar zenith angle (Seinfeld and Pandis, 2006)." L114

- You write "Available photons for photolysis reactions were calculated as a function of latitude and time of year ..." This should be explained in detail in the manuscript.

See previous comment.

Appendix A

- Units of the rate coefficients should be given.

We have added units to the rate coefficients table.

- Fluorotelomer aldehyde photodissociation: I tried to trace the rate coefficient for the reaction 1 (Appendix A), for which the value 1.5+-0.75E-22 (no units) is given, with reference to Young and Mabury (2010). Young and Mabury (2010) give two photodissociation cross sections for FTALs, 13.3E-20 (no error estimate) cm2 (Chiappero et al., 2006) and 5.4+-0.4E-20 cm2 (Solignac et al., 2007), at the maximum of the absorption spectrum. Young and Mabury (2010) do not give the photodissociation rate coefficient. How does the photodissociation rate coefficient 1.5+-0.75E-22 and its error estimate
The value of 1.5e-21 in the table is accounting for both the Solignac [2007] number that the reviewer quotes (5.4e-20) and the maximum full spectrum quantum yield of dissociation (0.04) from Sellevåg [2004]. These are combined to relate the total actinic flux to the dissociation of FTAL molecules. The uncertainty estimate was increased to 50% because we apply the values to longer chain homologues of the actual molecules from these experiments, and because of the scarcity of data.
Uncertainty and variability in atmospheric formation of PFCAs from fluorotelomer precursors

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Abstract. Perfluorocarboxylic Perfluoroalkyl carboxylic acids (PFCAs) are environmental contaminants that are highly persistent, bio-accumulative, and have been detected along with their atmospheric precursors far from emissions sources. The importance of precursor emissions as an indirect source of PFCAs to the environment is uncertain. Modeling studies have used degradation mechanisms of differing complexities to estimate the atmospheric production of PFCAs, and these differing mechanisms lead to quantitatively different yields of PFCAs under differing atmospheric conditions. 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. 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.

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, and estimate uncertainties in such calculations for urban, ocean, and Arctic conditions using polynomial chaos methods. We find that atmospheric conditions farther from pollution sources have both higher capacities to form long chain PFCAs and higher uncertainties in those capacities.

Our calculations of theoretical maximum yields indicate that under typical Northern Hemisphere conditions, less than 10% of emitted precursor may reach long-chain PFCA end products. This results in a possible upper bound of 2-50 t/yr of long-chain PFCA (depending on quantity of emitted precursor) produced in the atmosphere via degradation of fluorotelomer products. However, transport to high-yield areas could result in higher yields. While the atmosphere is a potentially growing source
of long-chain PFCAs in the Arctic, oceanic transport and interactions between the atmosphere and ocean may be relatively more important pathways to the Arctic for long-chain PFCAs.

KEYWORDS: PFCA, PFAS, FTOH, perfluoroalkyl, perfluorocarboxylic acids, per- and polyfluorinated chemicals

1 Introduction

Perfluorocarboxylic Perfluoroalkyl carboxylic acids (PFCAs) are environmental contaminants that are highly persistent, bio-accumulative (Martin et al., 2003a, b; Conder et al., 2008), and have been detected along with their atmospheric precursors far from emissions sources (Young et al., 2007; Shoeib et al., 2006; Stock et al., 2007) in snow (Xie et al., 2015), precipitation (Scott et al., 2006), and biota (Houde et al., 2006). Of particular environmental interest are the long-chain PFCA (lcPFCA, PFCAs of chain length greater than 7) homologues such as PFOA (8-Carbon chain), due to the increase of detrimental effects increased bioaccumulation with chain length (Martin et al., 2003a, b; Conder et al., 2008). PFCA 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. While lcPFCA are not regulated internationally, reducing lcPFCA emissions has been the focus of some national policy actions due to their detrimental health effects (Vierke et al., 2012), and as a result, direct emissions have been decreasing globally. At the same time, emissions of atmospheric precursors of PFCAs are rising (Wang et al., 2014a), leading to an increasing indirect source of PFCAs to the environment. These precursors, including fluorotelomer alcohols (FTOHs), react with atmospheric photochemical species (Ellis et al., 2003) in a multi-stage process to form PFCAs (Young and Mabury, 2010). However, the importance of precursor emissions as an indirect source of lcPFCA to the environment is uncertain. Estimated yields of PFCAs from precursors can vary based on differences in the formation mechanism assumed, quantitative uncertainty in reaction rate constants, and ambient concentrations of other atmospheric species. Here, we use a box model analysis to quantitatively estimate potential upper-limit atmospheric yields of PFCAs, incorporating uncertainty in the precursor degradation mechanism and variability of atmospheric PFCA formation due to photochemical background conditions.

Previous studies have estimated yields of lcPFCA from the degradation of FTOHs in the atmosphere (Yarwood et al., 2007; Wallington et al., 2006). However, studies have indicated that other emitted atmospheric precursors exist in the form of other fluorotelomer compounds, perfluoroalkyl sulfonamides (FOSAs), and perfluoroalkyl sulfonamidoethanols (FOSEs) (Young and Mabury, 2010; Wang et al., 2014a, b; Young et al., 2008; Butt et al., 2009). Rate coefficients for the reactions in the PFCA formation mechanism are uncertain, affecting estimated yields. The atmospheric formation of PFCAs depends on reactions of fluorinated intermediates (Waterland and Dobbs, 2007; Chiappero et al., 2006) with commonly studied photochemical species, such as HOx and NOx species, as well as
ultraviolet light. These species vary greatly over different environments in the atmosphere, affecting the quantity of lcPFCA produced.

Modeling studies have used degradation mechanisms of differing complexities to estimate the atmospheric production of PFCAs, and these differing mechanisms lead to quantitatively different yields of lcPFCAs under differing atmospheric conditions. Wallington et al. (2006) simulated the atmospheric degradation of 8:2 FTOHs using the IMPACT atmospheric chemistry model, finding that PFOA yields ranged from 1-10% depending on location and time. Yarwood et al. (2007) used a higher resolution atmospheric chemistry model over North America to estimate that degradation yielded approximately 6% PFOA on average, and much less than 1% PFNA. Schenker et al. (2007), using a global-scale multispecies mass-balance model with simplified chemistry, found that precursor transport and degradation could contribute to perfluorocarboxylates observed in the Arctic, and that rate constant uncertainty was an important contributor to uncertainty in their results (Schenker et al., 2007).

In our work, we evaluate PFCA formation with the most complete degradation mechanism to date to our knowledge, including the reactions presented in the studies of Wallington et al. (2006) and Yarwood et al. (2007), and the review of Young and Mabury (2010). 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. We use a box model analysis to simulate the atmospheric chemical fate of fluorotelomer aldehyde (FTAL), a common early product in the degradation of many of the different precursor species, including FTOHs. We quantitatively estimate the influence of uncertainty in rate coefficients for calculations of PFCA yields using polynomial chaos methods, which have been used previously in the context of chemical reaction mechanisms (Phenix et al., 1998) and atmospheric chemistry modeling in particular (Cheng and Sandu, 2009; Thackray et al., 2015). We further examine the influence of different atmospheric chemical conditions on upper-limit PFCA formation based on output from a three-dimensional chemical transport model. We conclude by estimating potential upper limits for atmospherically formed PFCAs from emitted precursors, and compare our yield results to observed atmospherically formed PFCAs.

2 Methods

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. We calculate yields of PFOA (8 Carbons) and PFNA (9 Carbons) from the degradation of 8:2 fluorotelomer precursors. We use prescribed concentrations of photochemical species from data sources described below. 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. Thus, our calculations represent an upper limit of the PFCA for-
mation capacity of the atmosphere at given photochemical conditions. We use the LSODE solver implemented in the "scipy" package of Python to solve the system of differential equations defined by this chemistry.

2.1 Mechanism and Box Model

In our box model, we use a precursor degradation mechanism which builds on the work of previous modeling efforts [Wallington et al., 2006; Yarwood et al., 2007] and includes reactions from recent literature [Young and Mabury, 2010]. The chemical reactions included are listed in Appendix A, and depicted in Figure 1. The mechanism defines the degradation of fluorotelomer aldehyde, which we use as a generic precursor as it is the first degradation product of emitted volatile fluorotelomer compounds such as FTOHs and FT-iodides. This FT-aldehyde can be oxidized by OH or photolyzed to form peroxy or acylperoxy radicals. These radicals, in turn, react with NO, NO2, RO2, and HO2 to form stable intermediates. These stable intermediates can again be radicalized by further reaction with OH and ultraviolet light, with more analogous radical reactions leading to either stable PFCAs or shorter chain intermediates. Reaction products which have chain lengths shorter than PFOA are neglected in our calculations.

We use a box model of the PFCA formation chemistry to calculate yields of PFOA and PFNA from precursor species. The single-box model simulates the chemical reactions discussed above, treating the concentrations of HOx, NOx, Cl, and RO2 as constant and neglecting non-chemical loss processes such as wet and dry deposition. Simulations begin with a unit of precursor species and are carried out until all of the initial precursor has reached one of the reaction end-points (PFNA, PFOA, or shorter-chain PFCAs). The yield of each end species is defined as the fraction of the initial precursor that forms that species.

2.2 Variability of PFCA formation

To quantify the variability of PFCA formation capacity due to variations in the atmospheric chemical background of the Northern Hemisphere, we use photochemical species concentration output from the chemical transport model GEOS-Chem [Bey et al., 2001]. We use concentrations of OH, HO2, NO, NO2, and temperature output from a GEOS-Chem version 9.01.02 full chemistry simulation of the years 2006 and 2007 after a one year spin up.

We calculate RO2 concentrations based on concentrations of methane, ethane, and propane from the GEOS-Chem simulation and a pseudo-steady state approximation:

\[
[RO_2] \approx \frac{[CH_4][OH]k_{CH_4+OH} + [C_2H_6][OH]k_{C_2H_6+OH} + [C_3H_8][OH]k_{C_3H_8+OH}}{[NO]k_{NO+RO_2} + [HO_2]k_{HO_2+RO_2}}
\]  

(1)

Available photons for photolysis reactions were calculated based on a scaling by the position of the sun as a function of latitude and time of year based on an assumption of clear sky conditions.
and a peak actinic flux of 1x10^{15} photons cm^{−3} s^{−1} at 90.0 degrees solar zenith angle (Seinfeld and Pandis, 2006). We use daily GEOS-Chem output concentrations from winter (January) and summer (July) of 2007 as a representative sample of the variability of atmospheric conditions in the Northern Hemisphere.

For the photochemical conditions corresponding with each surface grid box and time of the GEOS-Chem output, we perform a box model run to calculate yields and formation times of PFOA and PFNA. This results in 1656 chemical environments for each of the summer and winter conditions.

### 2.3 Uncertainty Propagation

We calculate the **parametric** uncertainty in yields and formation times for PFCA formation in three case environments. We use conditions chosen from the above GEOS-Chem output data set representing three distinct photochemical environments as representative test cases. We have selected one each of urban, Arctic, and ocean environments for their distinctive PFCA formation behaviors. The photochemical concentrations of each environment are detailed in Table 1. The urban environment is located over urban China, and is characterized by high NO\textsubscript{x} concentrations. The ocean environment, in contrast, is located over the equatorial Pacific Ocean and is characterized by very low NO\textsubscript{x} concentrations. The environment illustrative of Arctic PFCA formation is located over Greenland, and is much colder and has a moderate level of NO\textsubscript{x}.

We use polynomial chaos (PC) methods to propagate uncertainty from rate constants to yields calculated by the box model. PC methods create a polynomial expansion representation of the model to propagate uncertainty in inputs to the outputs at low computational cost while being able to represent non-linear responses of outputs to model input parameters, as well as interactions between input parameters (Thackray et al., 2015; Lucas and Prinn, 2005; Cheng and Sandu, 2009). The PC-based estimator uses orthogonal polynomials to approximate GEOS-Chem model output as a function of model inputs. The polynomial expansion of the model output to be estimated takes the form

\[
\eta(\zeta) = \alpha_0 + \sum_{j=1}^{d} \sum_{k=1}^{M} \alpha_{j,k} H_j(\zeta_k) + \sum_{k=1}^{M-1} \sum_{l=k+1}^{M} \beta_{k,l} H_1(\zeta_k)H_1(\zeta_l) + \ldots + \text{Order}(d \geq O > 2) \quad (2)
\]

where the estimator \( \eta \) of degree \( d \) is a function of the polynomials \( H_j \) of order \( j \), the \( M \) variables \( \zeta_k \) representing model inputs, the expansion coefficients \( \alpha_{j,k} \) and \( \beta_{k,l} \), and higher order coefficients. Not shown in the equation are cross terms of degree \( >2 \), which include the product of up to \( d \) Hermite polynomials of different variables, analogous to the second order cross terms shown. In this study, we truncate the polynomial after third order. To obtain the expansion coefficients, one model run at a unique set of inputs is performed for each term in the equation (Tatang et al., 1997). The set of inputs for the model runs for each degree’s terms are the values corresponding to the roots of the next degree’s polynomials. The outputs of these model runs and the corresponding sets of input values are used to set up a system of equations to solve for the expansion coefficients (Lucas and Prinn).
We use the polynomial estimator to directly infer properties of the uncertainty distribution of model output (in this case theoretical maximum fractional yields of PFOA and PFNA) without relying on Monte Carlo methods, which is accomplished using the analytical forms of the mean and variance from the polynomial coefficients (Lucas and Prinn, 2005). We also calculate the portion of the total output variance contributed by each rate constant using the expansion coefficients (Lucas and Prinn, 2005; Cheng and Sandu, 2009). We carry out a second-order expansion in the 40 uncertain reaction rate constants to calculate uncertainty distributions of PFOA and PFNA yields and attribute the importance of each reaction rate constant to the resulting parametric uncertainty.

2.4 Environment Categorization

In order to categorize the differences in photochemical environments, we use the DBSCAN clustering algorithm (Ester et al., 1996) to find clusters in summer average OH-HO$_2$-NO concentration space. These three species were chosen because they are the most common non-fluorinated reactants in the modeled chemistry, and because they led to the delineation of the observed behavior in yield-time space apparent by visual inspection (see Section 3.4). The DBSCAN algorithm is density-based, clustering based on the proximity of nearest neighbors in the chosen parameter space. The algorithm requires a priori values for its two parameters, $\varepsilon$, which roughly describes the size of the "neighborhood" around a datum, and $N_\varepsilon$, the number of other data that must be within that neighborhood to be considered a cluster. The clustering is relatively insensitive to choice of $N_\varepsilon$ (Ester et al., 1996), but the number of clusters found in the data set depends on the value of $\varepsilon$ chosen. We choose an $N_\varepsilon$ value of 10 and the $\varepsilon$ value (0.3) that gives the smallest number of clusters >1 for simplicity in categorization. This results in two major clusters accounting for >85% of the data, with the remaining data unclustered.

3 Results

We calculate the variability in PFOA and PFNA theoretical maximum yields for summer and winter Northern Hemisphere conditions, and quantify the parametric uncertainty in these theoretical yields for three representative test cases. We also investigate the distinct chemical regimes in the formation of PFNA in different regions of the atmosphere under average summer conditions.

3.1 Variability in yields due to photochemical environment

Figure 2 shows histograms of theoretical maximum yields of PFOA and PFNA for each of the photochemical environments from GEOS-Chem output. Each count in the histogram corresponds to a calculation of yields carried out at the conditions from a single day and Northern Hemisphere grid-box (latitude-longitude location) from the GEOS-Chem output. For PFOA during the summer, the majority of photochemical environments result in yields of between 1% and 10%, with approxi-
mately a quarter of the environments yielding <1% and a third of environments yielding between 10% and 30%. During the winter, the peak of PFOA yields remains between 1-10% but many more environments yield <1% and fewer yield >10% compared to during the summer.

PFNA, on the other hand, sees a peak less than 1% during the summer, but shows a third of its environments between 1% and 10%, with a small fraction of environments leading to yields higher than 80%. During the winter, PFNA formation skews toward very low yields of <0.1%. The long tails of PFNA formation environments are discussed further in Section 3.4. Previous work (Yarwood et al., 2007) quantified yields of PFOA and PFNA over the United States, but the extreme capacities to yield lcfPFCAs in remote low-NO$_x$ environments have been previously unquantified.

3.2 Uncertainty in yields due to rate constant uncertainty

Figure 3 shows uncertainty in PFOA and PFNA yields due to uncertainty in the rate constants in the degradation mechanism. 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). Under oceanic conditions far from NO$_x$ sources, the PFOA yield is approximately 20%, with an uncertainty range of approximately 3%, and the PFNA yield is more than 80%, with an uncertainty range of approximately 5%. Under Arctic conditions, PFOA yield uncertainty ranges between 18% and 22%, and PFNA shows a distribution ranging from 17% to 20%. For both species, and especially PFNA, the range of yields due to differing photochemical conditions is much larger than the range of yields due to uncertainty at any given conditions. 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.

3.3 Rate coefficient contributions to yield uncertainty

Fractional contributions of individual reactions’ rate coefficient uncertainties to the resulting yield uncertainty for PFOA and PFNA formation are summarized in Table 2. Most reactions in the mechanism contribute to uncertainty similarly for PFOA yield under urban conditions, with reaction 16 having the largest contribution. The rate of this reaction between poly-fluorinated peroxy radicals and RO$_2$ radicals to form a poly-fluorinated alcohol is one of the main factors determining whether the yielded product is PFNA or a shorter chain PFCA (including PFOA), which makes it important for the uncertainties in yields for both of those end products. For ocean conditions, reaction rate constants 15, 16, 36 and 37 dominate the contributions to PFOA yield uncertainty. Arctic conditions show reaction 37’s rate constant uncertainty also playing a large role, but reaction 34 also makes a substantial contribution. Reactions 15 and 16 represent a branching in the degradation chemistry where fluorinated peroxy radicals can either branch toward PFNA formation or PFOA and shorter chain PFCAs. Likewise, reactions 34, 36, and 37 are at a branching point where shorter peroxy radicals can either react to form PFOA or even shorter chain PFCAs.
PFNA yield uncertainties are dominated by a different subset of the reaction mechanism for the Arctic environment, and see a contribution from a large number of reaction rates for the urban and ocean cases, led by reactions 16 and 2 (reaction of OH with the initial precursor), respectively. In the Arctic, reaction rate constant 16 uncertainty dominates, with reaction 14 (another peroxy radical reaction) also contributing significantly. 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 RO$_2$ with poly- and per-fluorinated peroxy radicals are the dominant sources of theoretical maximum yield uncertainties for PFOA and PFNA, leading sources in the degradation chemistry.

3.4 Regime behavior in PFNA yields and formation times

Figure 4 shows calculated PFNA yield for each GEOS-Chem grid box and associated time of formation for summer conditions, with DBSCAN algorithm clusters in the OH-HO$_2$-NO space of the sample of summer atmospheric photochemical conditions. Two distinct regimes appear in the plotted space, one in which yield is low across formation times, and one in which longer formation times are associated with higher yields. As figure Figure 4 shows, the clusters in OH-HO$_2$-NO space correspond to regimes of formation for PFNA, and to spatial regions of the atmosphere. Each of the two clusters respectively compose the majority of each of the two regimes in PFNA yield - time of formation space. Figure 4(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. Within the lower-latitude mode, PFNA yield increases with decreasing NO concentrations, with the lowest yields occurring over land in more polluted areas and the highest yields occurring over the oceans far from NO$_x$ sources.

4 Discussion

We find a wide variety of theoretical maximum yields for both PFOA and PFNA across the Northern Hemisphere’s photochemical environments. With many regions yielding less than 1% of each due to the presence of large enough quantities of NO$_x$, but PFOA yields of up to 40% and PFNA yields of up to 80% in some areas, the specific photochemical environment has a strong effect on the capacity of the atmosphere to yield lcPFCAs from the degradation of emitted precursors. We find that the parametric uncertainty in these theoretical maximum yields depends on the environment as well, but is at most on the order of a few percent, much smaller than the variability caused by the diversity in photochemical environments.

We find two distinct regimes of PFNA formation capacity in the atmospheric environment, which correspond to photochemical environments found in the Arctic and at lower latitudes, respectively.
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. The second regime, on the other hand, shows that at lower latitudes there is a large range of both yields and formation times, and that longer formation times are associated with higher theoretical maximum yields. Within this regime, the higher the concentration of NO, the shorter the formation time and the lower the yield capacity. Figure 5 illustrates this behavior, showing the flux through different reactions in the chemical mechanism over the course of a box model run at the conditions of the three representative environments introduced in Section 2.3. The nodes in the diagram represent intermediate or end-product species in fluorotelomer degradation, while the lines represent the reaction fluxes, with the thickness of the lines proportional to the flux. Figure 5(a) and (b) show that at lower latitudes the amount of NO present strongly drives fluxes towards either short chain PFCAs (Urban, high-NO conditions) or long chain PFCAs (Ocean, low-NO conditions). The reactions of peroxy radicals with NO are too fast in the presence of substantial NO to allow branching toward PFNA or PFOA formation.

The highest theoretical maximum yields and longest formation times are associated with conditions over the oceans far from sources and far from common photochemical pollution sources. Emissions of lcPFCA precursors into polluted air masses reduces the potential for those precursors to form lcPFCAs. Put another way, emissions of precursors in otherwise less-polluted regions are conducive to more lcPFCA formation per precursor emitted.

The calculations that we present are of lcPFCA theoretical maximum yields, and are the upper limits of PFOA and PFNA formation for given atmospheric conditions. In the atmosphere, non-chemical loss processes that we neglect in our model limit actual lcPFCA yields compared to their theoretical maxima. In the case of PFNA, as the areas with highest theoretical maximum yields are associated with the longest formation times, they will see larger discrepancies between theoretical and actual yields than areas with lower theoretical maximum yields. Although regions far from NO sources have the greatest capacity for PFNA formation, they also are most vulnerable to having concentrations of degradation intermediates reduced by wet deposition and scavenging before the degradation has reached an end product (e.g. over the equatorial oceans).

We calculate the theoretical maximum yields of lcPFCAs from precursor degradation under many atmospheric conditions, but the degradation mechanism is indicative of daytime chemistry. In the Arctic during the summer this is not problematic, but in the winter it neglects the possibility of significant nighttime chemistry involving species such as N2O5 and H2O2 that to our knowledge has not been studied. Future research could put theoretical or experimental constraints on the possible importance of these reactions.

With respect to theoretical maximum yields in different seasons, winter conditions lead to lower yields of both PFNA and PFOA, sometimes by orders of magnitude. [Young et al., 2007] report a similar seasonal dependence from the Devon Ice Cap, with summer concentrations of PFOA and PFNA
being an order of magnitude higher than winter concentrations in the accumulated snow profiles. For the years 2004 and 2005, the average winter PFNA concentration in those snow measurements is 18 times smaller than the average summer concentration, and for PFOA the winter average is 7 times smaller. In our calculations, those same ratios over the Canadian Arctic are 18 and 10, respectively. As the long-chain PFCA deposited on the Devon Ice Cap is most likely atmospherically generated, this suggests consistency between our calculations of PFNA and PFOA theoretical yields and observational evidence of lcPFCA yielded through formation in the atmosphere.

The importance of the photochemical environment to lcPFCA formation, particularly the importance of the presence of NO\textsubscript{x}, means that future air pollution reductions or increases could impact atmospheric lcPFCA yields. For instance, large reductions in NO\textsubscript{x} emissions would lead to more lcPFCA products. However, given our results, we find that NO\textsubscript{x} concentration reductions would have to be on the order of magnitude scale to affect theoretical maximum yields significantly.

We estimate uncertainty ranges in theoretical maximum yields for PFOA and PFNA under the ocean case conditions to be 17-22% and 78-85%, respectively, with most of the uncertainty for PFOA stemming from uncertainty in rate constants at a branching point in the degradation mechanism. In the Arctic case conditions, PFOA maximum yield has a similar value and level of uncertainty as for ocean conditions, while PFNA yields have a much lower value and slightly lower level of uncertainty. Again, under these conditions, the majority of the uncertainty is due to uncertainty in two peroxy radical reaction rate constants at branching points in the mechanism. Better understanding the quantitative relationship between rate constants at these branching points will have the greatest effect on reducing the parametric uncertainty in theoretical maximum yields.

We quantify the parametric uncertainty in theoretical maximum yields, which depend exclusively on the rate constants. In the atmosphere, where deposition can play an important role in lcPFCA formation, many other sources of uncertainty for yields will arise, such as rates of deposition, frequency of rainout and washout events, solubility and aqueous chemistry of intermediate species, among others. While the uncertainty due to rate constants is quantifiable based on the chemistry used in our calculations, any missing reactions in the degradation chemistry will be unquantifiable. If our mechanism is incomplete due to currently unidentified reactions, our estimates of uncertainty would underestimate the full uncertainty of the chemistry. Our estimates of the variability of lcPFCA theoretical maximum yields in the atmosphere are also uncertain due to uncertainty in the photochemical conditions used, which are output from the GEOS-Chem model. The uncertainty in GEOS-Chem calculations of photochemical environment is not quantified here, nor is the uncertainty due to the model grid box size’s inherent smoothing of photochemical extremes.

The maximum yields calculated above allow us to estimate potential upper limits on the amount of atmospherically produced long-chain PFCAs given the emitted precursor quantities. The current estimate \cite{Wang2014} of volatile 8:2 fluorotelomer compound global releases has an upper bound
of 500 t/yr for the year 2010, the only year for which such a detailed estimate is available. Given the theoretical maximum yields we have calculated, this translates to 50 t/yr of lcPFCAs produced atmospherically based on median yield values from our calculations. This may be an overestimate, however, considering the spatial distribution of theoretical maximum yields. In regions that precursors are emitted (over continental North America, Europe and Asia), theoretical maximum yields are less than 1%. If the precursors and intermediates reside in this type of environment for extended periods of time, the upper limit of atmospheric lcPFCAs could be 5 t/yr or lower. However, larger yields can result when precursors are transported to higher-yield environments. These estimates of upper limit atmospheric production scale linearly with emissions, so emissions rates lower than the upper bound estimates would lead to correspondingly lower atmospheric production maxima. 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 6 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 NO₃ 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 PFCAs to form.

We quantify the theoretical maximum yields of formation of lcPFCAs 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 FOSeEs are found along with FTOHs in the remote atmosphere (Shoeb 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.

The uncertainty and variability estimates that we present indicate quantitatively that the most important piece of information for calculating atmospherically formed PFCAs is their chemical 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 \( \text{HO}_2-\text{NO}_2 \) photochemistry and PFCAs themselves has further value over the previous work.

Future calculations with a detailed chemical transport model that also accounts for both deposition processes and transport in the atmosphere would allow for a best estimate of total lcPFCA production in the atmosphere over time. While the U.S. EPA Stewardship Program strives to greatly reduce lcPFCA precursors emitted due to American manufacturers, there remains the possibility of growth of precursor production in Asia in the future, meaning that atmospheric lcPFCA formation could become increasingly important as a source globally and to the Arctic. 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 \( f_{\text{PFCA}} \) of PFCA formation from the “unzipping” step of the mechanism is

\[
\begin{align*}
\frac{Y(8)}{1 - Y(9)} = f_{\text{PFCA}} (1 - \sum_{i=x+1}^{\text{longer}} Y(i))
\end{align*}
\]

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

\[
Y(X) = f_{\text{PFCA}} (1 - \sum_{i=x+1}^{\text{longer}} Y(i))
\]

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, Table 3 shows the extension of the Arctic case where the theoretical maximum yields of PFNA and PFOA are 18% and 20%, respectively.

Wallington et al. [2006] estimated 0.4 t/yr of PFOA entering the Arctic due to atmospheric production via 8:2 FTOH degradation; the amount entering the Arctic is less than half of global atmospheric PFOA production. This was calculated assuming 1000 t/yr of FTOH emitted to the atmosphere, which is twice the current upper bound of total fluorotelomer emissions to air. Wania [2007] estimated that the amount of atmospherically generated PFCAs deposited in the Arctic peaked in 2005 at 0.154 t/yr, and that 11-21 t/yr is transported to the Arctic via the ocean. Both of these studies estimate atmospherically generated quantities of lcPFCAs which fall reasonably beneath our calculated theoretical maxima. Our results indicate, however, that the region over the oceans is the leading atmospheric environment for lcPFCA formation, meaning that transport to the Arctic via the ocean can be importantly affected by lcPFCAs formed atmospherically at lower latitudes. A detailed coupled
atmosphere-ocean model could give important insights to future studies. 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).

5 Conclusions

We calculate PFOA and PFNA formation theoretical maximum yields for the degradation of precursor species at a representative sample of atmospheric conditions, and estimate uncertainties in such calculations for urban, ocean, and Arctic conditions. We find that atmospheric conditions farther from pollution sources have both higher capacities to form long chain PFCAs and higher uncertainties in those capacities. The greatest uncertainty reductions through reaction rate determinations can be achieved by better quantifying rate constants at the branching points of the degradation chemistry. We find that there are distinct regimes of PFNA formation behavior in different photochemical environments, dictated by the quantities of HO\(_x\) and NO\(_x\) species, but less variability in the formation of PFOA.

While we study the daytime chemistry in detail, future studies should investigate the role of nighttime chemistry in lcPFCA formation. The role of non-chemical removal processes from the atmosphere is also an important part of atmospheric lcPFCA formation, and its environmental connection to yields of formation should be investigated.

Our calculations of theoretical maximum yields indicate that most likely less than 10% of emitted precursor can reach lcPFCA end products in the Northern Hemisphere, even ignoring non-chemical losses. This results in an upper bound of 2-50 t/yr of lcPFCA (depending on quantity of emitted precursor) produced in the atmosphere via degradation of fluorotelomer products. Only a fraction of that is destined to directly deposit in the Arctic. While the atmosphere is a potentially growing source of lcPFCA in the Arctic, oceanic transport and interactions between the atmosphere and ocean of directly emitted, and to a lesser extent low-latitude atmospherically generated, PFCAs are likely more important pathways to the Arctic for lcPFCA.

Acknowledgements. This work was supported by the U.S. National Science Foundation Arctic Natural Sciences Program (1203526) and a fellowship from the National Science and Engineering Research Council of Canada (to C.P.T.).
Appendix A: List of reactions
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant expression</th>
<th>uncertainty</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) C8F17CH2C(O)H + hv350 → C8F17CH2O</td>
<td>1.5x10^{-21} [cm^2 photon^{-1}s^{-1}]</td>
<td>7.5x10^{-22}</td>
<td>1</td>
</tr>
<tr>
<td>(2) C8F17CH2C(O)H + OH → C8F17CH2C(O)OH</td>
<td>2.0x10^{-12} [cm^3s^{-1}]</td>
<td>0.4x10^{-12}</td>
<td>~</td>
</tr>
<tr>
<td>(3) C8F17CH2C(O)H + Cl → C8F17CH2C(O)OO</td>
<td>1.9x10^{-11} [cm^3s^{-1}]</td>
<td>0.2x10^{-11}</td>
<td>~</td>
</tr>
<tr>
<td>(4) C8F17CH2C(O)OO + NO2 → C8F17CH2C(O)OONOO2</td>
<td>1.1x10^{-11} [cm^3s^{-1}]</td>
<td>0.1x10^{-12}</td>
<td>~</td>
</tr>
<tr>
<td>(5) C8F17CH2C(O)OONOO2 → C8F17CH2C(O)OO</td>
<td>2.8x10^{10}exp(T/-3580) [s^{-1}]</td>
<td>0.2x10^{16}</td>
<td>3</td>
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<tr>
<td>(6) C8F17CH2C(O)OO + NO → C8F17CH2O</td>
<td>7.1x10^{-12}exp(T/340) [cm^3s^{-1}]</td>
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<td>3</td>
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<tr>
<td>(7) C8F17CH2C(O)OO + H2O → C8F17CH2O</td>
<td>3.1x10^{-13}exp(T/1040) [cm^3s^{-1}]</td>
<td>0.3x10^{-13}</td>
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<tr>
<td>(8) C8F17CH2C(O)OO + H2O → C8F17CH2C(O)OH</td>
<td>1.2x10^{-13}exp(T/1040) [cm^3s^{-1}]</td>
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<td>3.1</td>
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<tr>
<td>(9) C8F17CH2C(O)OO + CH3O2 → C8F17CH2O</td>
<td>1.8x10^{-12}exp(T/500) [cm^3s^{-1}]</td>
<td>3.6x10^{-13}</td>
<td>~</td>
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<tr>
<td>(10) C8F17CH2C(O)OONOO2 + CH3O2 → C8F17CH2C(O)OH</td>
<td>2.0x10^{-13}exp(T/500) [cm^3s^{-1}]</td>
<td>4.0x10^{-14}</td>
<td>2</td>
</tr>
<tr>
<td>(11) C8F17CH2C(O)OH + OH → C8F17CH2O</td>
<td>2.0x10^{-12}exp(T/920) [cm^3s^{-1}]</td>
<td>0.6x10^{-12}</td>
<td>~</td>
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<tr>
<td>(12) C8F17CH2C(O)OH + OH → C8F17C(O)H</td>
<td>1.1x10^{-12}exp(T/920) [cm^3s^{-1}]</td>
<td>0.3x10^{-12}</td>
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<tr>
<td>(13) C8F17CH2O + H2O → C8F17CH2OHOH</td>
<td>4.1x10^{-13}exp(T/750) [cm^3s^{-1}]</td>
<td>0.4x10^{-13}</td>
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<tr>
<td>(14) C8F17CH2O + NO2 → C8F17CH2O</td>
<td>2.8x10^{-12}exp(T/300) [cm^3s^{-1}]</td>
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<td>3</td>
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<tr>
<td>(15) C8F17CH2O + CH3O2 → C8F17CH2O</td>
<td>1.9x10^{-14}exp(T/390) [cm^3s^{-1}]</td>
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<tr>
<td>(16) C8F17CH2O + CH3O2 → C8F17CH2O</td>
<td>7.6x10^{-14}exp(T/390) [cm^3s^{-1}]</td>
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<tr>
<td>(17) C8F17CH2OH + OH → C8F17C(O)H</td>
<td>1.02x10^{-13}exp(T/350) [cm^3s^{-1}]</td>
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<td>4</td>
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<tr>
<td>(18) C8F17CH2OH + Cl → C8F17C(O)H</td>
<td>6.5x10^{-13}exp(T/350) [cm^3s^{-1}]</td>
<td>1.0x10^{-13}</td>
<td>2</td>
</tr>
<tr>
<td>(19) C8F17CH2OH + H2O → C8F17CH2O</td>
<td>4.0x10^{-12}exp(T/200) [cm^3s^{-1}]</td>
<td>1.0x10^{-12}</td>
<td>2</td>
</tr>
<tr>
<td>(20) C8F17CH2O → C8F17OO</td>
<td>2.5x10^{-12} [cm^3s^{-1}]</td>
<td>0.1x10^{-12}</td>
<td>4</td>
</tr>
<tr>
<td>(21) C8F17C(O)H + hv350 → C8F17OO</td>
<td>1.6x10^{-21} [cm^3 photon^{-1}s^{-1}]</td>
<td>0.12x10^{-21}</td>
<td>1</td>
</tr>
<tr>
<td>(22) C8F17C(O)H + OH → C8F17C(O)O</td>
<td>6.1x10^{-13} [cm^3s^{-1}]</td>
<td>0.5x10^{-13}</td>
<td>1</td>
</tr>
<tr>
<td>(23) C8F17C(O)H + Cl → C8F17C(O)OO</td>
<td>2.8x10^{-12} [cm^3s^{-1}]</td>
<td>0.7x10^{-12}</td>
<td>1</td>
</tr>
<tr>
<td>(24) C8F17C(O)H + H2O → C8F17C(O)HOH</td>
<td>1.0x10^{-13} [cm^3s^{-1}]</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(25) C8F17C(O)HOH + OH → C8F17C(O)OH</td>
<td>1.22x10^{-13} [cm^3s^{-1}]</td>
<td>0.26x10^{-13}</td>
<td>1</td>
</tr>
<tr>
<td>(26) C8F17C(O)HOH + Cl → C8F17C(O)OH</td>
<td>5.8x10^{-13} [cm^3s^{-1}]</td>
<td>0.9x10^{-13}</td>
<td>1</td>
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<tr>
<td>(27) C8F17C(O)OH + NO2 → C8F17C(O)OO</td>
<td>1.1x10^{-11} [cm^3s^{-1}]</td>
<td>0.1x10^{-11}</td>
<td>3</td>
</tr>
<tr>
<td>(28) C8F17C(O)OO + NO2 → C8F17C(O)OO</td>
<td>2.8x10^{-10}exp(T/-3580) [s^{-1}]</td>
<td>0.2x10^{-10}</td>
<td>1</td>
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<tr>
<td>(29) C8F17C(O)OO + NO → C8F17OO</td>
<td>8.1x10^{-12}exp(T/270) [cm^3s^{-1}]</td>
<td>0.6x10^{-12}</td>
<td>3</td>
</tr>
<tr>
<td>(30) C8F17C(O)OO + H2O → C8F17C(O)OH</td>
<td>3.1x10^{-13}exp(T/1040) [cm^3s^{-1}]</td>
<td>0.4x10^{-13}</td>
<td>3.1</td>
</tr>
<tr>
<td>(31) C8F17C(O)OO + H2O → C8F17OO</td>
<td>1.2x10^{-13}exp(T/1040) [cm^3s^{-1}]</td>
<td>0.4x10^{-13}</td>
<td>3.1</td>
</tr>
<tr>
<td>(32) C8F17C(O)OO + CH3O2 → C8F17OO</td>
<td>1.8x10^{-12}exp(T/1040) [cm^3s^{-1}]</td>
<td>3.6x10^{-13}</td>
<td>2</td>
</tr>
<tr>
<td>(33) C8F17C(O)OO + CH3O2 → C8F17C(O)OH</td>
<td>2.0x10^{-12}exp(T/1040) [cm^3s^{-1}]</td>
<td>4.10^{-14}</td>
<td>1</td>
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<tr>
<td>(34) C8F17OO + NO → C8F17O</td>
<td>2.8x10^{-13}exp(T/300) [cm^3s^{-1}]</td>
<td>1.4x10^{-13}</td>
<td>3</td>
</tr>
<tr>
<td>(35) C8F17OO + H2O → C8F17O</td>
<td>4.1x10^{-13}exp(T/500) [cm^3s^{-1}]</td>
<td>0.4x10^{-13}</td>
<td>3</td>
</tr>
<tr>
<td>(36) C8F17OO + CH3O2 → C8F17O</td>
<td>2.7x10^{-13}exp(T/-470) [cm^3s^{-1}]</td>
<td>1.9x10^{-13}</td>
<td>3</td>
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<tr>
<td>(37) C8F17OO + CH3O2 → C8F17OH</td>
<td>1.0x10^{-13}exp(T/660) [cm^3s^{-1}]</td>
<td>0.6x10^{-14}</td>
<td>3</td>
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<tr>
<td>(38) C8F17C(O)F + H2O → C8F17C(O)OH</td>
<td>3.86x10^{-12} [cm^3s^{-1}]</td>
<td>0.7x10^{-6}</td>
<td>1</td>
</tr>
</tbody>
</table>

1 Young and Mabury 2010, 2 JPL Evaluation 2015 using hydrocarbon analog, 3 Wallington et al. 2006, 4 Yarwood et al. 2007
References


Table 1. Case environment conditions. Photochemical concentrations in $\text{cm}^{-3}$, temperatures in K

<table>
<thead>
<tr>
<th></th>
<th>Urban</th>
<th>Ocean</th>
<th>Arctic</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>$2 \times 10^{10}$</td>
<td>$1.7 \times 10^{7}$</td>
<td>$1 \times 10^{8}$</td>
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<tr>
<td>OH</td>
<td>$2 \times 10^{7}$</td>
<td>$5.4 \times 10^{6}$</td>
<td>$1.6 \times 10^{7}$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>$2 \times 10^{11}$</td>
<td>$5 \times 10^{7}$</td>
<td>$1 \times 10^{8}$</td>
</tr>
<tr>
<td>HO$_2$</td>
<td>$9 \times 10^{9}$</td>
<td>$1 \times 10^{8}$</td>
<td>$3.7 \times 10^{5}$</td>
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<tr>
<td>RO$_2$</td>
<td>$8 \times 10^{6}$</td>
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<td>$2.2 \times 10^{6}$</td>
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<td>$h\nu$</td>
<td>$9.4 \times 10^{14}$</td>
<td>$9.76 \times 10^{14}$</td>
<td>$1 \times 10^{15}$</td>
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<tr>
<td>Temperature</td>
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<td>299</td>
<td>265</td>
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Figure 1. Diagram of reaction mechanism used in box model. Each line represents a reaction, with color of the line indicating the photochemical family of the non-fluorinated reactant. Numbers correspond to specific reactions listed in Appendix A.
Figure 2. Histograms of variability in PFOA (a and b) and PFNA (c and d) theoretical maximum yields for both summer (a and c) and winter (b and d) conditions. Each count corresponds to a GEOS-Chem grid-box’s output photochemical environment.

Figure 3. Uncertainty distributions of PFOA (left) and PFNA (right) yields for urban, ocean, and Arctic conditions. In both cases, urban yields are much less than 1%. 

Table 2. Fractional yield uncertainty contributions of rate constants (%)

<table>
<thead>
<tr>
<th>Rxn #</th>
<th>PFOA_urban</th>
<th>PFOA_ocean</th>
<th>PFOA_Arctic</th>
<th>PFNA_urban</th>
<th>PFNA_ocean</th>
<th>PFNA_Arctic</th>
<th>Reaction</th>
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<tr>
<td>1</td>
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<td>&lt;1</td>
<td>&lt;1</td>
<td>2</td>
<td>&lt;1</td>
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<td>C8F17CH2C(O)H + hν -&gt; C8F17CH2O0</td>
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<tr>
<td>2</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>10</td>
<td>&lt;1</td>
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</tr>
<tr>
<td>6</td>
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<td>&lt;1</td>
<td>&lt;1</td>
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<td>2</td>
<td>&lt;1</td>
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<tr>
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<td>&lt;1</td>
<td>&lt;1</td>
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<td>2</td>
<td>&lt;1</td>
<td>C8F17CH2C(O)OO + HO2 -&gt; C8F17CH2O0</td>
</tr>
<tr>
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<td>7</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>2</td>
<td>&lt;1</td>
<td></td>
<td>C8F17CH2C(O)OO + HO2 -&gt; C8F17CH2C(O)O0</td>
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<tr>
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<td>&lt;1</td>
<td>&lt;1</td>
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<td>C8F17CH2C(O)OO + RO2 -&gt; C8F17CH2C(O)O0</td>
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<tr>
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<td>&lt;1</td>
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<td>2</td>
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<td>&lt;1</td>
<td>&lt;1</td>
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<td>2</td>
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<tr>
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<td>57</td>
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<td>&lt;1</td>
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<td>C8F17OO + NO -&gt; C8F17O</td>
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<td>C8F17OO + RO2 -&gt; C8F17O</td>
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<td>C8F17OO + RO2 -&gt; C8F17OH</td>
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</table>

Table 3. Theoretical maximum yield calculations extended to other precursor lengths and product lengths for an environment with PFNA yield of 18% and PFOA yield of 20%.

<table>
<thead>
<tr>
<th>Product</th>
<th>12:2 Precursor</th>
<th>10:2 Precursor</th>
<th>8:2 Precursor</th>
<th>6:2 Precursor</th>
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<td>0.00</td>
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<tr>
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<tr>
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</tr>
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<td>0.03</td>
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</tr>
<tr>
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<td>0.04</td>
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<td>Remainder</td>
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<td>0.12</td>
<td>0.20</td>
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Figure 4. (a) Each photochemical environment plotted in yield-formation time space. Color indicates membership of a cluster in OH-HO$_2$-NO space. Black circles indicate unclustered points. (b) Geographic location of clusters. Colors correspond to the same clusters in both figures.

Figure 5. Total flux through each reaction for the degradation mechanism for urban (a), ocean (b) and Arctic (c) conditions. Each line represents a reaction, with color of the line indicating the photochemical family of the non-fluorinated reactant, and the thickness of the line is proportional to the total flux through the reaction over the course of a simulation.
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.