

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

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 NO_x 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 HO_x, NO_x, 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 $[OH] = 1E6 \text{ cm}^{-3}$, $[Cl] = 1E5 \text{ cm}^{-3}$, 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 in 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 IcPFCAs 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 NO_x 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

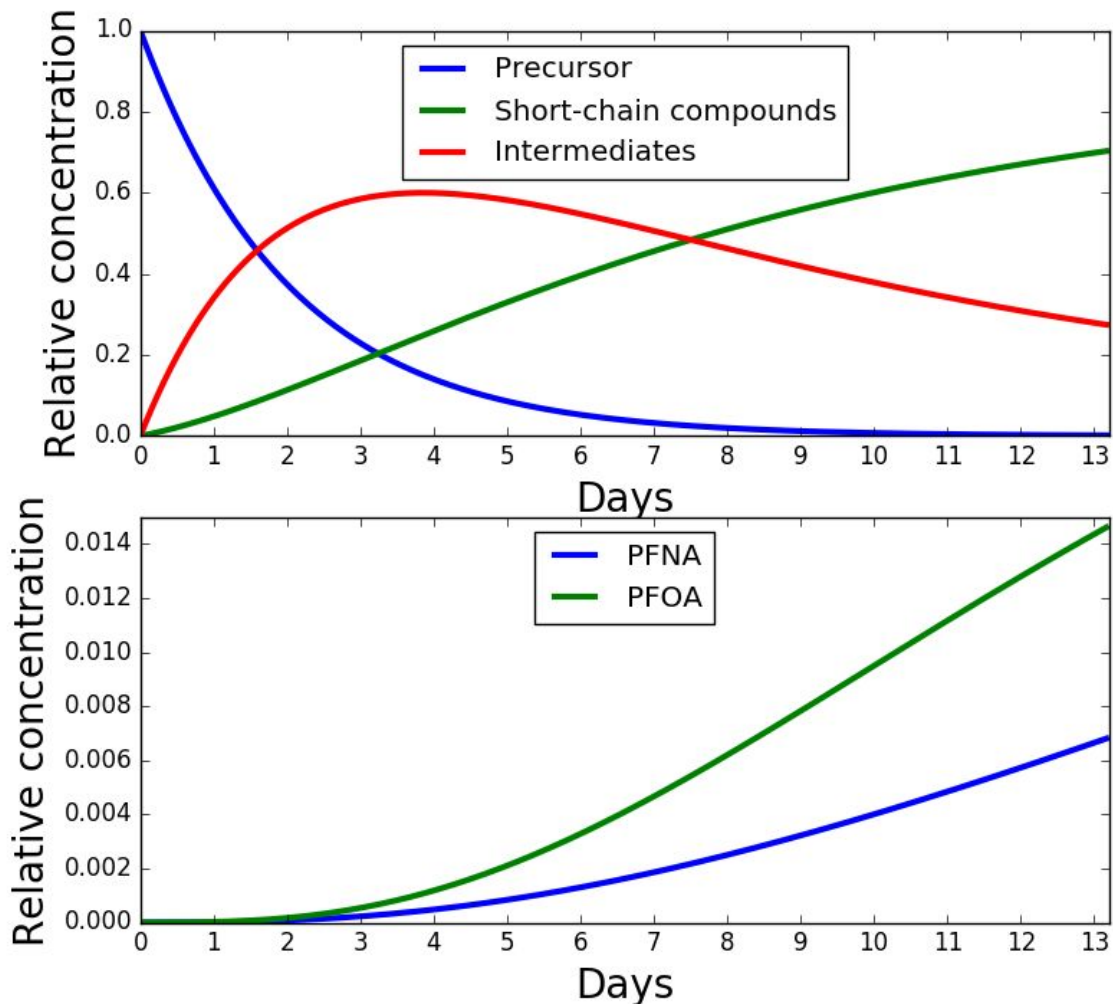


Figure 5. Fluorotelomer precursor chemical fate along HYSPLIT trajectory through summertime photochemical environments. After two weeks, yields of PFOA and PFNA are approximately 1.5% and 0.7%, respectively, with more than 20% of the initial precursor still in an intermediate form which will undergo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

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

Used.

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 1×10^{15} photons $\text{cm}^{-3} \text{s}^{-1}$ 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 $\text{cm}^{-2} \text{s}^{-1}$, not photons $\text{cm}^{-3} \text{s}^{-1}$. 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 ($5 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$) and summer ($8.9 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$) 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 1×10^{15} photons $\text{cm}^{-2} \text{ s}^{-1}$ 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 $1.5 \pm 0.75 \times 10^{-22}$ (no units) is given, with reference to Young and Mabury (2010). Young and Mabury (2010) give two photodissociation cross sections for FTALs, 13.3×10^{-20} (no error estimate) cm^2 (Chiappero et al., 2006) and $5.4 \pm 0.4 \times 10^{-20} \text{ cm}^2$ (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 $1.5 \pm 0.75 \times 10^{-22}$ and its error estimate

arise?

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 Sellevag [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.