Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-679-RC2, 2016

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Uncertainty and variability in atmospheric formation of PFCAs" *by* Colin P. Thackray and Noelle E. Selin

Anonymous Referee #2

Received and published: 25 October 2016

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

Printer-friendly version

Discussion paper

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.

Review

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 [OH] = 1E6 cm-3, [Cl] = 1E5 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. 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.

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. How does this uncertainty compare with the fairly

small uncertainty arising from uncertainty in the rate coefficients? 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." 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.

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. 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.

Recommendation

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 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 PFCAs from from fluorotelomers, despite the formation taking place on time scales during which air parcels are transported and experience different chemical conditions. 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. If this is not possible I recommend rejection in favor of a re-submission in which a more appropriate modeling approach, such as the 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.

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.

- 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). 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).

- 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.

Appendix A

- Units of the rate coefficients should be given.

- 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 arise?

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-679, 2016.

Printer-friendly version

Discussion paper