

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

Anonymous Referee #1

Received and published: 21 September 2016

Summary comments: The title and abstract of the paper were highly promising. 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. 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 sulfonamides (FOSAs), perfluorooctane sulfonamidoethanols (FOSEs), 10:2 FTOH etc. and miss to discuss these uncertainties in the discussion. 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

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

Specific comments: Line 25: perfluoroalkyl carboxylic acids is now the preferred name. Line 28: no year given in Scott et al. Line 29: Define precisely what you mean by "long-chain PFCAs" Line 30: rephrase "increased detrimental effects". I presume the authors mean bioaccumulation potential or toxicity or both? Lines 44-50: Authors miss to discuss other important precursors (see above). 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? 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. Lines 200-215: It is very hard to follow the reaction scheme; an overview figure would have been useful here. Lines 170-230: It would be useful to point exactly what is the novel contribution in the results. What does this study add to previous studies by e.g. Yarwood et al. 2007 nearly a decade ago? They already showed how NO_x in populated urban affects PFOA yields. Line 241-242: Explain what you mean by "different conditions within the Arctic"? 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? 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

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and Chemistry, Vol. 29, No. 8, pp. 1689–1695). Also it is well known that perfluorooctanesulfonyl fluoride (POSF)-based precursors can form PFCAs and levels of these POSF-based precursors (e.g. FOSEs) have not declined since the 3M phase-out.

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