Atmos. Chem. Phys. Discuss., 10, C4465–C4469, 2010
www.atmos-chem-phys-discuss.net/10/C4465/2010/

Atmospheric
Chemistry
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Discussions

Interactive comment on "Pathways of PFOA to the Arctic: variabilities and contributions of oceanic currents and atmospheric transport and chemistry sources" *by* I. Stemmler and G. Lammel

Anonymous Referee #1

Received and published: 25 June 2010

The paper by Stemmler and Lammel presents the first use of a coupled atmosphere-ocean global circulation model to describe the fate of perfluorooctanoic acid (PFOA). The Authors use the model to attempt to describe transport of PFOA by ocean and atmosphere and to elucidate the relative importance of primary and secondary sources of PFOA to the Arctic. The fact that the majority of industrially-produced PFOA ends up in the ocean is undisputed. Thus, this advanced model is useful to accurately predict the fate and transport of PFOA in the ocean. In particular, findings related to transport to the Arctic that differ from previous, simpler models are important in understanding and predicting PFOA contamination in the Arctic. However, the use of a sophisticated model for describing atmospheric sources and transport is questionable. This is described in detail below, along with other revisions required prior to final publication.

Models of PFOA fate up to this point have differed greatly due to their assumed inputs with respect to emissions and physical properties. Since the physical properties of PFOA are poorly described, it is difficult to model the relative ocean/atmosphere primary transport in a quantitative way. Considerable debate has centred around the pKa of PFO(A) and the subsequent impact on air/water partitioning. In this work, the Authors do not explicitly treat the dissociation of PFOA and instead claim it is described by the air-sea exchange parameters, but no further discussion is given. A value is given for the Henry's law constant of PFOA in Table 1, but there is no indication as to where this number came from or what the uncertainties associated with it may be. More discussion of the assumptions made regarding this particular property, as well as a sensitivity or error analysis, are required if the modeled results for primary transport through the atmosphere are to be of value.

The attempt to quantify the relative importance of primary and secondary atmospheric sources of PFOA should be removed. The additional complexity offered by this model is not useful in predicting the behaviour of fluorinated compounds in the atmosphere when so many other significant uncertainties exist. A model is only as good as its inputs, and in this case there are numerous omissions and simplifications that will lead to an erroneous output:

i) Incomplete precursors. The model includes only the 8:2 FTOH, when many other PFOA precursors are known to exist, including longer-chain FTOH congeners (10:2-18:2), fluorooctanesulfamido alcohols, as well as the full suite of fluorotelomer olefin, acrylate and iodide congeners. As many of these precursors are produced in high quantities and have been observed in the atmosphere, inclusion would certainly impact the yield of PFOA from secondary sources.

ii) Unknown emissions. Previous attempts to model the relative importance of primary and secondary atmospheric sources have differed due to their emission inputs. The emissions used here taken from Prevedouros et al (2006) were provided by industry and are not confirmable.

iii) Poorly defined chemistry. Many unknowns exist in the chemistry of precursor degradation to PFOA, particularly with respect to branching ratios. The Authors have used similar, but apparently simplified, chemistry to that modeled by Wallington et al. in 2006. However, this chemistry is incomplete given current knowledge. For example, the fate of the aldehyde (C_8F_{17}CHO) is considered here to be driven by reaction with hydroxyl radical. In reality, the primary fate of this aldehyde is likely photolysis to yield the perfluorinated radical, C_8F_{17} (Chiappero et al, 2006; Young and Mabury, in press). This chemistry is included in the Wallington et al. (2006) model and the reasons for its omission here are not clear. Further, the Wallington et al. (2006) model is missing a potentially important fate of the C_8F_{17}C(O) radical, which is loss of CO to form C_8F_{17} radical (Hurley et al, 2006). Lastly, the fate of C_8F_{17}OH is critical to the formation of PFOA, yet is not well understood. The instability of perfluorinated alcohols in the bulk phase means this reaction is unstudied in the lab and, thus, subject to significant uncertainty.

Specific comments:

Page 11580, line19: Should read "…atmospheric aerosols, partitioning is empirically based…".

Page 11584, line 20: The product of reaction R3a should be the corresponding fluorotelomer carboxylic acid and not the perfluorinated aldehyde.

Page 11587, lines 3 and 24; page 11592, line 27: Question marks should be removed.

Page 11588, lines 15-25: The authors should state their calculated atmospheric flux of primary PFOA in order to better compare with other studies.

Page 11589: It is not immediately obvious what is meant by AO1, etc. It would aid readers if these were earlier defined as sampling points from the Yamashita et al (2008)

study.

Page 11589, line 10: Should read "…in water samples at AO1…".

Page 11592, line 25: Should read "No PFOA observations in Arctic winter air have been reported."

Page 11593: Wet deposition is discussed and comparisons should be made with environmental precipitation data, such is that found in Scott et al (2006) and Dreyer et al (2010). Further, the model suggests a deposition maximum in the winter in the Arctic, which is contrary to analysis of snow samples from the Canadian High Arctic (as well as two other models). The Authors mention that there is a disagreement, but ignore the fact that one of the studies is empirical. They then state in the conclusions that PFOA transport is preferable in winter without even a qualifying statement. This is misleading when empirical evidence indicates the opposite.

Page 11594, lines 5-9: A depositional flux from Young et al (2007) of 0.27 tonnes per year is quoted. It is incorrectly stated that this flux was based on a single measurement from the Devon Ice Cap in 2004. In fact, this flux is from 2005 and based on the mean of four measurements from ice caps across the Canadian Arctic.

Page 11594, line12: "…are formed from precursors" is incorrect based on the parameters here. It should read "…are formed from 8:2 FTOH".

Page 11595, line 6: Should read "…through the Canadian Archipelago/Davis Strait reflects neither the outflow…".

Reference 3: Should read "Sulbaek Andersen, M.P." and not "Andersen, M.P.S.".

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 11577, 2010.