

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

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hithoughtfulcommentsandsuggestionstoimprovethequalityofthemanuscript.Listedbelowareourresponses(*italicized text*)

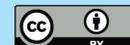
The paper by Stemmler and Lammel presents the first use of a coupled atmosphere-ocean global circulation model to describe the fate of perfluorooctanoic acid (PFOA). The Authors use the model to attempt to describe transport of PFOA by ocean and atmosphere and to elucidate the relative importance of primary and secondary

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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.

Indeed, the origin of the Henry coefficient, K^H , used was accidentally not specified in the manuscript. The Henry coefficient was derived from the dimensionless air-water partitioning coefficient, K_{aw} , ($K_{aw} = 10^{-3}/(RTK_{aw})$, with R = universal gas constant, T = temperature) which was adopted from a physico-chemical data base and software following Arp and Goss, 2009. The temperature dependence of K_{aw} is described using the enthalpies of vapourisation and solution (Table 1). The uncertainty for the derived temperature dependent Henry coefficient, $K^H(T)$, propagating from variation in parameters used in various data bases corresponds to approximately a factor of 2

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(see Arp and Goss, 2009). This uncertainty will be specified in the revised version. $K^H(T)$ is used to describe phase partitioning in cloudy air and volatilisation from the sea surface (two-film model, fugacity formulation; Liss and Slater, 1974). The process parameterisations used, as far as not described in the manuscript itself, were presented in Semeena et al., 2006, and Guglielmo et al., 2009.

The effective Henry's law coefficient, K^{H*} , a function of the pK_a ($K^{H*}(T) = K^H(T) \times (1 + K_a/c_{H^+})$ with $K_a =$ PFOA dissociation constant and $c_{H^+} =$ acidity of the aqueous phase), was used to account for the non-dissociated acid as the volatile species in seawater for the calculation of the volatilisation rate. $pK_a = 2.8$ was adopted (Table 1). However, considerably lower values, -0.5 – 0.0 , are currently discussed (Goss, 2008; Burns et al., 2008; Arp and Goss, 2009). PFOA fugacity from seawater and, hence, the volatilisation rate from the sea surface would be dampened by its stronger acidity of up to a factor of 2000 were the lowest, currently discussed pK_a value adopted. However, volatilization from the sea surface is a negligible source of PFOA in air. Therefore, PFOA concentration in air is hardly influenced by volatilisation from the sea surface: Given the lower estimate of the volatilisation rate, the global volatilisation flux from sea to air would be 0.0015 kg a^{-1} , corresponding to $5 \cdot 10^{-6} \%$ of the total PFOA flux from surfaces, instead of 3 kg a^{-1} or 0.01% of the total PFOA flux from surfaces.

As cloudwater pH is not calculated in the model, the Henry's law coefficient was not adjusted to PFOA dissociation equilibrium as a function of cloudwater pH (effective Henry's law coefficient). In consequence, in- and below-cloud scavenging was underestimated and, therefore, lifetime in air is possibly overestimated in the model world.

In summary the effect of uncertainties of physico-chemical properties on PFOA multicompartamental fate and transport is a tendency to overestimate the atmospheric burden and lifetime and, hence, atmospheric transport. This will partly compensate for neglect of precursors (other than 8:2 FTOH, see below).

The origin and the uncertainty of the value of K^H will be specified in a revised version.

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Possible implications for the conclusions on PFOA multicompartamental fate and transport will be explained and specified in a revised version.

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:

We certainly agree with the general statement on modelling in the context of deficient knowledge. However, compared to earlier attempts to simulate the relative importance of primary and secondary atmospheric sources of PFOA (Wallington et al., 2006; Schenker et al., 2008) the here used model setup makes use of a general circulation model with a higher spatial resolution. The study does not attempt nor even address to describe the general behaviour of fluorinated compounds, but has a very focused objective, i.e. (besides others) the meridional atmospheric long-range PFOA transport in the northern hemisphere as formed from one main precursor. The choice of a chemistry model imbedded in an atmosphere general circulation model is useful for the objective of the study, as expectedly (a) better representing the large scale dynamics and should be capable to better resolve the transport pathways from mid to high latitudes, and (b) produce a realistic inter-annual variability of the dynamics. Furthermore, (c) higher spatially and temporally resolved oxidant distributions promise to lead to correspondingly higher resolved distributions of secondary PFOA in air and, subsequently, deposited to land and sea surfaces. The inter-annual variability and, therefore, the influence of dynamics on chemical budgets can be addressed with longer simulations. This option will be emphasized in the Summary and conclusions section of a revised version.

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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.

We agree. The yield of PFOA from all secondary sources was not targeted, but was unintended suggested in the Introduction and in the Summary and conclusions. All conclusions drawn refer to one precursor only, 8:2FTOH. This will be clarified by re-phrasing the respective statements and adding an explanatory sentence to the Emissions section in a revised version.

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.

We agree, the emission scenario chosen is clearly deficient, however, not necessarily less accurate than other emission scenarios used in the past. This scenario was chosen for the sake of comparability with other model studies' results, which had used the same emission scenario (Armitage et al., 2006; Wania, 2007; Schenker et al., 2008). This way, complementary insights are possible, while it would be impossible to attribute differences in model results to the model setup in the case of differing emission scenarios.

In the chosen scenario PFOA is emitted in the northern mid latitudes. Main emitters are located in Central Europe (Northern Italy, Belgium), Japan, and in North America in the US Midwest and St. Lawrence water shed. As the accurate locations of the emission sources were unknown an assumption was made about the location within and the distribution of emissions among these source countries. Discrepancies from

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reality as a consequence of inaccurate location are expected mostly in the source regions. Long-range transport to remote (receptor) regions, which is the focus of the study, on the other hand is significantly less sensitive to the uncertainty in source location. In particular, the uncertainty in longitudinal direction within these countries are expected to be negligible on the long term.

iii) Poorly defined chemistry. Many unknowns exist in the chemistry of precursor degradation to PFOA, particularly with respect to branching ratios.

The atmospheric chemistry of perfluorinated compounds (PFCs) in general and of the 8:2 FTOH in particular is certainly not consolidated regarding the uncertainties in rate coefficients and branching ratios (besides other). Instead, laboratory kineticists have been exploring this chemistry since only recently and substantial progress is expected to be achieved in the near future. It was not within the scope of our study to explore the sensitivity of PFOA distributions and fluxes towards existing uncertainties in the understanding of the chemical sources and sinks (also in other compartments than air), which could be the focus of a study using a comprehensive and chemically detailed atmospheric and/or multicompartment chemistry box model. The approach of our study is to use a simplified atmospheric chemistry in combination with a sophisticated representation of atmospheric and oceanic large-scale transports, atmospheric and geospheric physical features (clouds, aerosols, land surfaces, soil properties), and intercompartmental mass-exchange processes. The simplified chemistry should capture the main features of the current state of the art. A similar approach, albeit lacking the multicompartmental dimension, is common for other fields of global atmospheric modelling, such as e.g. the global scale study of secondary organic aerosol formation (Kanakidou et al., 2008; besides others). As the current state of the art in representation of the atmospheric chemistry of PFCs is necessarily tentative, a similar future modelling study, which would make use of consolidated knowledge of atmospheric chemistry, would certainly promise to deliver essential added value.

The usage of a simplified chemistry was not explicitly stated in the Introduction section, which should be done in a revised version in order to better clarify the approach used.

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 (C₈F₁₇CHO) 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, C₈F₁₇ (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.

The chemistry modeled in our study is indeed slightly simplified, namely (and only) with regard to neglection/consideration of the photolysis channel of C₈F₁₇CHO (as pointed out by the reviewer). This deviation from the chemistry modeled by Wallington et al. was indeed not mentioned in the manuscript, which was accidentally. The reasons for neglection were as follows: The absorption spectrum and a photodissociation quantum yield of the substance in question, perfluorononanal, C₈F₁₇CHO, were not determined (or not reported to our knowledge). One reference suggested by the reviewer, Young and Mabury, in press 2010, is (still) not published or otherwise accessible. An estimate for the photodissociation channel could eventually be based on data measured for short-chain (C₁ – C₅) perfluoroaldehydes, for which ultraviolet-visible absorption cross sections (C₁ – C₄; Hashikawa et al., 2004) and quantum yields for photolysis (C₁ – C₅; Sellevåg et al., 2004; Chiappero et al., 2006) were reported. The corresponding photolysis products, C₈F₁₇ and C₈F₁₇H, would differ from the products of the reactions considered (R4, R5). However, the effective quantum yield of photolysis of CF₃CHO under pseudo-natural conditions is low (≤ 0.02 ; Sellevåg et al., 2004) and the quantum yields of the C₃ – C₄ perfluoroaldehydes are smaller than those of C₁ – C₂ perfluoroaldehydes (Chiappero et al., 2006). This reasoning would be included in condensed form in a revised version.

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Further, the Wallington et al. (2006) model is missing a potentially important fate of the C₈F₁₇C(O) radical, which is loss of CO to form C₈F₁₇ radical (Hurley et al., 2006).

The chemistry considered combines H-abstraction by OH from C₈F₁₇CHO and subsequent addition of molecular oxygen to C₈F₁₇CO (R4), although the yield of the latter step might deviate from 1, e.g. by decompositional loss of CO. However, this chemistry was not studied in the laboratory and the respective branching ratio of C₈F₁₇CO was not determined (or not reported to our knowledge). An estimate for the branching ratio could eventually be based on data measured for short-chain (C₂ – C₅) perfluoroacyl radicals, C_xF_{2x+1}CO (C₁ – C₄; Hurley et al., 2006). The significance of this decomposition channel is increasing from C₁ to C₄ at 298 K and 1000 hPa, suggesting large significance for longer perfluorinated alkyl chains at 298 K and 1000 hPa. However, significantly lower yields for this channel are expected for lower temperatures and lower pressures, i.e. for most geographic locations and altitudes, and no data to describe the temperature and pressure dependence are available for C_x, x > 1 (Hurley et al., 2006). We decided to neglect this possible reaction.

Lastly, the fate of C₈F₁₇OH 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.

Coverage of this uncertainty is not within the scope of our study which uses a simplified atmospheric chemistry in combination with a sophisticated representation of the physics (see above).

Specific comments:

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Page 11580, line19: Should read “. . .atmospheric aerosols, partitioning is empirically based. . .”.

Grammar/punctuation will be corrected. The phrasing is unambiguous, as the term ‘aerosol’ refers to the two-phase system of condensed-phase particles suspended in air.

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

Thank you; will be corrected.

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

These were technically caused. Now replaced by appropriate citation (Stock et al., 2007)

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

Will be given as range of absolute annual fluxes in a revised version.

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.

Yes; locations will be specified more clearly in a revised version.

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Page 11589, line 10: Should read “. . .in water samples at AO1. . .”.

Will be corrected.

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

Will be rephrased accordingly.

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).

Comparison of model results of atmospheric concentrations or concentration in wet deposition is only meaningful in remote regions, i.e. outside the PFOA source regions Central Europe, Japan, and the US Midwest and the St. Lawrence water shed, because of the uncertainty in the locations of the sources in the chosen emission scenario (see above). Therefore, concentrations observed in the Arctic were compared, while observational data obtained from measurements in the Northeastern US and Southeastern Canada (Scott et al., 2006) and Germany (Dreyer et al., 2010) were not compared. Furthermore, part of the data set from North America (1998-99 and 2002-04; Scott et al., 2006) and the entire data set from Germany (2007-08; Dreyer et al., 2010) could not be compared directly, because it is based on samples collected after the simulated period (ATC experiment, 1995-98).

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

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transport is preferable in winter without even a qualifying statement. This is misleading when empirical evidence indicates the opposite.

We appreciate the focussing of the discussion of these results. Indeed, the comparison between the empirical findings (Young et al., 2007) and the model results with regard to seasonality in PFOA concentration in total deposition should be spatially focused, as the observational data were obtained at one location, Devon Ice Cap in the Canadian Arctic archipelago. These represent the years 1995-2005. The seasonality in PFOA concentration in snow (spring-summer maximum) was attributed to the seasonality of wet deposition (minimum in winter), possibly in combination with the seasonality of photochemical formation from precursors (winter minimum, summer maximum; Young et al., 2007) . In the model, total deposition is dominated by wet deposition, too. The same seasonality is predicted by the model, but for only some of the simulated years, while no clear long-term seasonality of total deposition predicted by the model for this area and during the simulated years. Whether the model can capture the correct seasonality in this area could only be judged on basis of a longer simulation.

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.

Thank you; will be corrected.

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

Will be corrected.

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

Will be corrected

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

Will be corrected

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