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Atmospheric
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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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We thank reviewer #2 for her/his thoughtful comments and suggestions to improve the quality of the manuscript. Listed below are our responses (italicized text) to the comments and suggestions.

General
The model used is fully coupled, which means that it does not simulate a 'real'time period w.r. to the physical environment. This should be stated more clearly. Also the consequences of this fact for the interpretation of the results from both rather short (14 years and 4 years) experiments should be discussed more intense, e.g. how representative is the 4yr experiment given the known interannual to decadal variability in the atmospheric circulation (e.g. AO, NAO ...)

We agree the issue of model vs historic climate needs further clarification in the manuscript. The predicted state of the northern hemisphere atmosphere on the example of the AO index is 0.04 (± 1.05), while it was 0.14 (± 1.03) in reality during the years 1993-1998 (NOAA/NCEP, downloaded from their website [1]*. A figure of the monthly mean AO indices for 1993-1998 will be included in the Supporting Material of the revised manuscript (see Fig. 1).*

The predicted state of the near-Arctic ocean on the example of the Bering Strait showed an increase of the volume transport between 1998 and 2001, and a subsequent decrease until 2004, while the opposite, a decrease 1998-2001 followed by an increase until 2004, was found in reality (Woodgate et al. 2006). Corresponding statements will be included in a revised version.

The motivation for the two experiments, their expected benefit and problems should be addressed, too.

The analysis was split into 2 experiments to enable the quantification of oceanic currents and atmospheric transports separately. As the ATC experiment does not resolve oceanic currents PFOA is transported exclusively via the atmosphere in this experiment. In a single experiment including both, precursor chemistry and oceanic currents, the amount of PFOA in the Arctic ocean would result from both atmospheric and oceanic transport, and an analysis as shown in 3.3 would not have been possible, as the pollutant distribution looses its memory with regard to origin. This fact is mentioned in the experimental section by stating: '[..] allowing for the exclusive study of atmospheric transport.'It is an implication of this separation that ocean pollutant

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[1] http://www.cpc.ncep.noaa.gov/products/precip/CWlink/daily_ao_index/ao.shtml

figure-1.pdf

Fig. 1. Monthly mean AO indices for 1993-1998

transport is incompletely covered (see below).

Detailed remarks:

p 11585 l 22:
I do not understand what you want to say with ‘fully covered’, ’sum of AOT and ATC experiments’?

The meaning of ‘fully covered’was explained in the manuscript. in paragraph (l22ff): Oceanic transport is not fully covered, as in the AOT experiment deposition of FTOH originating PFOA is not included, hence less PFOA is transported in the oceans than would be in reality. In the ATC experiment, on the other hand, which includes deposition of PFOA from FTOH no oceanic currents are considered in the model. Atmospheric pollutant transport on the other hand is completely covered, as PFOA is not returning to the atmosphere once it is deposited into the ocean, hence although the ATC experiment does not include oceanic currents, atmospheric transport is fully covered. For more volatile compounds neglecting oceanic currents would imply generating non realistic atmospheric transport, as oceanic currents redistribute the substance in the ocean and thereby affect also re-volatilisation into the atmosphere. Will be slightly rephrased in a revised version.

p 11585 l 25:
‘Background concentrations’...do you mean ‘initial concentrations’?

We agree, the term ’initial concentrations’ is more appropriate in this context.

p 11586 l 15 ff:
The use of both, log KOC and KOC values, in the ms is confusing, please explain and

then use only one of both throughout the ms.

In the reference (Higgins & Luthy, 2006) a value of K_{oc}*=115 ml* g^{-1} *was published. As is it more convenient to use log*K_{oc} *values after introducing the value it is only referred to as log*K_{oc}*. There is only this one paragraph in the MS where both notations are used, apart from figure legends (Fig.8,9). These will be modified accordingly in a revised manuscript. Recent experimental evidence, not available by the time of the model experiments and submission of the study (Sakurai et al., 2010) suggests that the choice of the high* K_{oc} *to mimick effective sorption of an amphiphilic substance beyond partitioning to the bulk organic phase is very close to reality. This, too, should be added to a revised version to substantiate the scenarios.*

p 11587 l 15ff:
What is meant with ‘coarse emission scenario’, if the predicted distributions are very different from reality in the source latitudes, how can we expect them to be of any use even further away from the source?

PFOA is emitted in the northern mid latitudes. The reported main emittors 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 by the time this study was undertaken an assumption was made about the location within and the distribution of emissions among these source countries. Discrepancies from 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. Furthermore, despite obvious deficiencies of this scenario the same emission scenario as in other modelling studies (Armitage et al., 2006; Wania, 2007; Schenker et al., 2008) was used for the sake of comparability. 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.

p 11587 l 19ff:
The seasonal cycle seems to be significant, of which value are the snapshot-like model observations comparisons, esp. since there is no information if the model shows a similar seasonal cycle as the observations? Discuss this please and include thoughts on interannual variability.

It is correct that campaign based observational data can not give insights into the seasonal or interannual variability of pollutant levels, which are indeed important features for assessing the fate of PFOA. However, no long-term monitoring data are available for PFOA. Interannual variability of air and ocean concentrations of PFOA are so far largely unknown. The only exceptions are a snow pit in the Canadian Arctic, covering 1995-2005 (Young et al., 2007; see this discussion, reply to the comments of reviewer #1) and one year of aerosol sampling at a rural site in Germany, 2007-08 (Dreyer et al., 2010). The latter data cannot be compared, because these are based on samples collected after the simulated period (ATC experiment, 1995-98). At this state of research numerical modelling provides the only source of evidence.

Would it be possible to present a table or map instead of listing ?

We considered that, but decided otherwise, as explanatory text would still be needed, because of the heterogeneity of the observational data sets.

P 11589 l9 ff:
Please explain the abbreviations ‘AO, etc ’for the stations.

We agree, mentioning only AO etc without explanation makes the sentence hard to read, the specific locations are included in brackets whenever AO1-5 are mentioned.

17 ff:
The text is somewhat cryptic: ‘the subsurface is explained...’??
Which ‘independent deep water current’are you talking about, the Denmark Strait Overflow Water? Is this a hypothesis or what leads you to this conclusion? Please be more specific!

These are citations of how Yamashita et al 2008 explain the vertical stratification. For making it more clear in line 19 after ‘the subsurface is explained’a ‘by Yamashita et al. 2008 ’will be included in a revised version.

I cannot see a ‘similar stratification’, AO2 is completely different, AO1 differs at depth and also shows different levels.

This statement does not refer to AO1, but only to site AO2. The whole paragraph reads:

‘Modeled concentrations, as well as observed ones at AO2, decrease until 500 m, and remain constant down to 2000 m. In waters below 2000m PFOA concentration increases for observations, but decreases in the model results. Yamashita, 2008 suggest that water masses from the surface down to 2000m were well mixed due to their convective formation. The subsurface is explained by Yamashita et al. 2008 by a decrease caused by the influx of the melt-water rich Labrador current, and the increase in larger depths by the presence of an independent deep water current carrying higher amounts of PFOA. A similar stratification is observed in the model results, except for the deep water current, that decreases concentrations in waters below 2000 m.’
Here, ‘A similar stratification ’refers to the fact that also in the model results PFOA concentrations decrease until 500 m and remain relatively constant below 500 m Predicted and observed concentrations at AO2 differ largely only below 2000 m. But this is clearly stated in the paragraph. In contrast to AO1 which shows from 500 m to 2500m concentrations of approx. 50 pg L^{-1}, as at the surface, for AO2 a significant

decrease below the surface can be seen in both observations and model results, which justifies the conclusion of a ‘similar stratification’.

I am missing a discussion of the sense/no-sense of such a localized (point wise) comparison of observations and data. This is very difficult to interpret, and observations are very sparse. Please discuss what ‘can’we learn from this comparison and what ‘do’we learn from it.

We recognize the obvious deficiency of model evaluation efforts based on point-to-point comparison, both spatially and temporally. Such a comparison is at best justified in lack of monitoring data - which, however, is the general state of affairs with regard to organic ocean pollutants. It allows to validate spatial gradients and, eventually, temporal trends (not in the case of PFOA) qualitatively and predicted concentrations on an order-of-magnitude basis. Such a statement will be included in a revised version in order to clarify the scope of the comparison of predicted and observed data.

p 11594
l15 ff:
How can a result covering just fourteen years of arbitrary atmospheric circulation be used to draw the conclusions? With regard to the oceanic flow this is even more questionable than for the atmospheric one.

We drew conclusions on the relative significance of atmospheric and oceanic meridional pollutant transports from northern mid to high latitudes. The physical aspects of these transports refer to present day climate and should be well represented, as validated in the context of model intercomparison exercises of the AGCM (Roelofs et al. 2001) and the OGCM (Jungclaus et al. 2006) used. The chemical aspects, however, refer to the historically unique (transient) emissions of the pollutant and its precursors during the simulated period. Therefore, the conclusions are historically *explicit and cannot be taken as representative for previous or future periods. To this end model experiments using adapted emission scenarios and, eventually, state of climate would be needed.*

p 11595 and ff
Your use of the word ‘transport’is sometime misleading, please chose words which clearly discriminate between the water transport and the transport of PFOA. Again, the discussion of specific years or periods is problematic since the time is just determined by your source function, not the flow fields. This has to be critically discussed at least.

The fact that historically concrete years refer to the emissions is mentioned several times in the manuscript. A clarifying sentence will be added to the conclusions of the revised version.

l 4/5:
Why does the Norwegian Coastal Current carry 50-80% ? It is fed by Baltic Sea outflow and Norwegian runoff. What does the general comparison with ‘other pollutants’tell us, since they may have completely different source distributions?

In this context, the comparison with other ocean pollutants is valid, as it had been shown that the main import of pollutants to the Arctic is via the Norwegian coastal current (NCC; Barrie et al., 1992; Macdonald et al., 2000). In the model world, it is neither fed by Baltic Sea outflow, nor by Norwegian runoff, but by transport of PFOA emitted into the Atlantic at the mouth of the St. Lawrence river or into the North Sea. Here, not the sources of the pollutants for the NCC are discussed but the 4 possible pathways to the Arctic are compared to each other. These insights would also apply for other ocean pollutants, as the NCC would similarly play a major role. The pollutants referred to will be identified in a revised version and the implications clarified.

l 9:
Do you mean the overflow? Please be more concrete. ‘This outflow...’which one, the subsurface flow? What about the surface, is there no outflow?

‘This outflow’refers to the outflow out of the Denmark Strait, which is PFOA transport integrated over all model levels. Aakrog, 1987, showed by analysing radionucleid tracer distributions that some northward moving waters are returned by a subsurface outflow on the East coast of Greenland. This finding was used here to explain the fact that there is outflow out of the Denmark Strait. Outflow at surface level was not quantified, but is certainly much less significant.

l16-18
I do not understand this sentence.

The sentence the reviewer refers to is : ‘Due to topography, bathymetry, and salinity distribution this transport, which accounts for 2-8% of the total PFOA transport into the Arctic Ocean, is a net inflow.’The sentence will be rephrased in a revised version:
‘This transport, which accounts for 2-8% of the total PFOA transport into the Arctic Ocean, is a net inflow driven by a mean sea level slope directed downwards to north (Overland and Roach 1987). This slope is primarily a consequence of a steric level difference between the North Pacific and the Arctic Ocean in the order of 0.5 m.’

p 11596
l 7:
which ‘inflow’the total?

For clearity ‘inflow via the Norwegian Sea or Davis Strait’will be added.

l 12:
What do you mean by ‘diverging inflow patterns’?

The sentence will be rephrased:
Moreover, as a consequence of the inflow patterns, which are inhomogeneous across longitude sections, and the Arctic ocean circulation a very inhomogeneous spatial distribution of PFOA evolves over the 54 years of model simulation.

l 14:
C4943
You are discussing experiment AOT, the reference to a 54 experiment (the ’spin up which produced the initial conditions?) is unclear here.

(AOT + spin-up) will be added in a revised version.

p 11597
l 1 ff
It is not possible that an imbalance of 1 Sv exists in the complete volume fluxes for the Arctic basins over a year (you can easily calculate what kind of sea level change would result from that). The fluxes must be balanced on short time scales. Either you madean error in the calculation of the fluxes or the model does not fulfill mass conservation(which I do not presume).

We very much appreciated this warning. The calculations were repeated and corrected results will be presented in the revised version. It turned out, that for part of the simulated year 2002 the file containing the velocities in horizontal directions was corrupt, leading to artificially high and low contributions of some month in 2002. This actually caused the apparent positive 2002 net stream function value. A corrected figure 9 was created and will be included into the manuscript (here: Fig. 2a). The general

statements do not change, but the resulting PFOA and volume transports are slightly different for the simulated year 2002.

Mention the meaning of the two KAC values in the caption. The reader is lost otherwise. Please chose different names (e.g. KOC1, KOC2)

It is unclear why the reviewer thinks the meaning of the K_{oc} values might be unclear. In the legend there are K_{oc}=115 ml g^{-1} and Koc=11500 ml g^{-1} values, which were introduced previously. A new definition of $K_{oc}1$ and $K_{oc}2$ on the other hand would be confusing. The K_{oc} values will be replaced by logK_{oc} values in a revised manuscript.

Fig. 9:
Please show a map with the sections.

A figure showing the locations of the sections will be included in the revised version (see Fig. 2b).

I guess the black line is the volume transport, please say so!

A corresponding statement will be added to the figure caption in a revised version of the manuscript.

Minor issues:
At several places in the ms I find question marks, which is exactly how I think about them. Please replace them.

This was caused by an inaccurate citation label in the Latex code of the manuscript, which will be corrected.

figure-2.pdf

Fig. 2. Time series of annual transports $[ta^{-1}]$ of PFOA (two substance scenarios) into the Arctic ocean and annual mean stream functions [Sv], (a.) locations of 4 cross sections surrounding the Arctic ocean, (b.) total and individual contributions through these cross sections.

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