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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Distributions, long term trends and emissions of four perfluorocarbons in remote parts of the atmosphere and firn air" *by* J. C. Laube et al.

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General comments

This is a nice study reporting the measurements of four longer chain (C4-C7) perfluorinated n-alkanes from a number of different sampling programs. The data tell a consistent story about increasing abundances of these chemicals over the past few decades related most likely to human-derived emissions, and I believe it will be of interest to readers of ACP. Comparisons are made to inventory-based emissions estimates and large differences are noted. I only have minor comments. One concern relates to the section on deriving past atmospheric trends from stratospheric measurements of the

chemicals (p. 4081-4082). The authors mention some limitations to this derivation (measurement precision is not as good), but they should also indicate the limitations of the technique they have chosen. One concern is the suggestion that mean age is a concrete quantity with only small errors (implied from their use of a linear regression to derive rates), when in fact a stratospheric air parcel represents of air with a distribution of ages that are not well defined. The authors have rightly not presented their firn data as discrete points with dates for this reason. Because similar processes are at play in the stratosphere, I would think it also quite suspect to plot the stratospheric data as discrete points with distinct ages. I would think it important to mention these caveats and the simplifications incorporated in the analysis so as to not mislead the reader into thinking the results of the analysis of this stratospheric air are particularly robust. Given these issues, it seems inappropriate to use any consistency in rates to suggest that the stratospheric lifetimes of these chemicals are long; Instead, this seems reasonable and appropriate to be taken as an assumption in the analysis. It also seems incorrect to presume that similar growth rates will be derived in the SH and globe if averaged over an 8-year period (line 8, p 4082).

Author response

Firstly we would like to thank you for this very thorough review which has helped to improve our manuscript. We agree that there are limitations to the stratospheric trend method and a respective statement has been added to the manuscript:

“However, it should be noted that there are uncertainties of this technique which we can not account for such as the unknown distribution of ages contained within a stratospheric air parcel.”

However, this method has been successfully applied to CF4 and C2F6 by Harnisch et al., 1996b giving very similar growth rates as compared to those derived from tropospheric archives in Muehle et al., 2010. For these reasons we have not changed the growth rate comparison with the Cape Grim record and only slightly modified the

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statement about the long lifetimes by exchanging “means” with “indicates” in “This also indicates that the two compounds do not have any significant sinks...” .

Referee comment

Figure 6, this latitudinal gradient for C5F12 during 27/10/2009 seems quite improbable. Did other predominantly NH-derived chemicals show this distribution, or could it represent a sampling/analysis issue?

Author response

We agree that the latitudinal gradient of C5F12 during those flights is unusual but have found no indications for a sampling or analysis issue. No other compounds were found to have a similar gradient for this flight. However, it should be noted that such flights only provide “snapshots” of the atmosphere on a particular day which are not necessarily representative for longer periods. Moreover the error bars only represent the 1 σ measurement uncertainties and within the 2 σ error bars (i.e. 95 % confidence interval) most of the gradient would be insignificant.

Referee comment

p. 4082, lines 19-21, were other trace gases measured that could provide information about stratospheric influences on particular samples?

Author response

Information is available for other trace gases and stratospherically influenced samples. However, due to the small growth rates and no sink reactions in the lower stratosphere the stratospherically influenced samples do not stand out in the case of the reported four compounds. Moreover we only use the tropical samples (within 20° of the equator) for comparison with other data sets. These can be considered as most representative for global tropospheric trends as they are unlikely to be influenced by stratospheric air due to the higher tropopause in this region. Therefore we feel a further discussion of stratospherically influenced samples would add little to the main messages of the

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paper.

Referee comment

p. 4083, it could be mentioned that errors in lifetime cannot reconcile the differences between the inventory emissions and those derived from atmospheric data.

Author response

The respective statement was complemented:

“But as the lifetimes of these compounds are on the order of several thousand years (IPCC, 2007; WMO, 2011), the sink reactions have a negligible influence on the derived emissions. For the same reasons errors in these lifetimes cannot reconcile any differences between the inventory emissions and those derived from atmospheric data.”

Referee comment

Figure 8. I would suggest that this figure be made into 2 panels showing the different compounds. I find it quite difficult to interpret as is. It would add useful context to provide, for example, the current annual fossil-fuel derived CO2 emission for comparison to annual or total cumulative PFC emissions (last paragraph). It also seems a bit surprising that no mention of the radiative forcing contributed by these chemicals is made. This would be a useful and fairly easy addition.

Author response

The numerical emission data was added to the supplementary material in order to ease the interpretation for the interested reader. A statement was added to the discussion section to provide more context and information on radiative forcings:

“When applying the radiative forcings from IPCC, 2007 (C4F10: 0.33 Wm-2ppb-1,C5F12: 0.41 Wm-2ppb-1,C6F14: 0.49 Wm-2ppb-1) and Bravo et al., 2010 (C7F16: 0.45 Wm-2ppb-1) to the mixing ratios observed at the end of 2010 at Cape Grim we derive a radiative forcing of 0.285 mWm-2 from the sum of the four compounds. This

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is only 0.017 % of the radiative forcing caused by anthropogenic CO2 in 2005 (IPCC, 2007) and we therefore conclude that their current contribution to global warming is comparably small."

Referee comment

Abstract: Line 12, the presence of a chemical in the stratosphere does not necessarily confirm that it has a "very long atmospheric lifetime"

Author response

The statement was altered to "with the data indicating that they have no significant sinks in this region.".

Referee comment

Abstract: Line 14-15, could be clearer, differ by five orders of magnitude among the measured compounds or between atmosphere- and EDGAR-derived values? It is the latter, of course, but this is clear only upon reader the paper.

Author response

The sentence was changed to "However, emissions of n-C4F10, n-C5F12 and n-C7F16 were found to differ by up to five orders of magnitude between our approach and the database."

Referee comment

Abstract: Line 17, Be clear that you are using 100-yr Global Warming Potentials here, in the text, and in Figure 10 caption.

Author response

"on a 100-year time horizon" was added in both cases.

Referee comment

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Abstract: Line 19, Emissions and CO2-eq emissions are quoted with no indication of certainty even though the 100-yr GWP of one chemical isn't known.

Author response

The statement was altered to "We estimate that. . ."

Referee comment

p. 4079, lines 16-20. how is it determined that the firn reconstruction through 2007 is OK but into 2008 is more uncertain? Is the point referring to seasonal influences on near-surface firn results?

Author response

Yes, and also on variability of samples collected at the surface.

Referee comment

p. 4080-81, lines 25-4. Are the authors suggesting that the errors in the reconstruction are actually larger than expressed by the dashed line in the figure? Some clarification is needed. It is also suggested that an inverse modeling approach gave similar results though they aren't discussed at all; were they within the uncertainties presented in the figure?

Author response

As explained in the figure caption the errors are derived as

"the sum of a) the firn air model maximum and minimum runs obtained by adding and subtracting the 1 σ measurement standard deviations to/from the firn data and b) the maximum deviation of the actual mixing ratios from the polynomial fitted to derive the NH trend."

Therefore the errors in the reconstruction can be larger than expressed by the dashed line when considering the 2 σ measurement standard deviations instead. The inverse

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modelling approach “gave results within the uncertainties presented in the figure” and this statement was added to the respective paragraph.

Referee comment

I find that the supplemental information contains useful and worthwhile information that adds to the paper. It might be worth mentioning the degree to which an isotopic impurities would affect the inventory vs atmosphere-based emissions figures (very negligibly, I presume). Is there a reason points instead of lines are used to express growth rates from fits in Figure S3?

Author response

We have found no indications for isotopic, isomeric or other impurities in these compounds (pure and atmospheric) to date except in the case of n-C7F16 where the uncertainty range was expanded accordingly. Points are being used instead of lines in Figure S3 as the respective growth rates are annual averages.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 4073, 2012.