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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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Author response

Thank you for your valuable comments which have helped to improve our manuscript. We have included a citation and a comparison to your work in the revised version:

"Finally it is notable that a work with a similar scope appeared in Atmos. Chem. Phys. Discuss. on the same day as ours (Ivy et al., 2012)."

"We have also compared our SH mixing ratios at the end of 2010 to the 2011 globally averaged background atmospheric mole fractions reported in the simultaneously pub-

lished work of Ivy et al., 2012. They find comparable mixing ratios of 0.18 ppt for C4F10 (our value: 0.171 ppt) and 0.12 ppt for C5F12 (our value: 0.141 ppt). However, in addition to possible calibration scale differences, the limitations of this comparison due to the above mentioned differences in collection dates and averaging methods should be noted."

"Ivy et al., 2012 report a comparable globally averaged mixing ratio of 0.28 ppt for 2011."

"Again, Ivy et al., 2012 report a comparable globally averaged mixing ratio of 0.12 ppt for 2011."

Comment

Section 2 - Experimental Methods - Is the instrument response linear over the entire range of samples measured? Were any linearity experiments done to assure there were no non-linearities due to preconcentration?

Author response

An experiment was carried out to ensure the linearity of the analytical system and the following text was added to the supplementary material.

"To determine the linearity of the response behaviour of the analytical system a static dilution series was prepared by diluting an unpolluted NH air sample collected in 2009 at Niwot Ridge near Boulder, USA (containing 0.177 ppt of C4F10, 0.136 ppt of C5F12, 0.257 ppt of C6F14, and 0.103 ppt of C7F16) with Research Grade Nitrogen (obtained from BOC Gases, UK) in stainless steel canisters. Five dilutions were prepared with dilution factors of 1.00, 0.672, 0.458, 0.236 and 0.00. Within the uncertainties of the dilution factors and measurement uncertainties (less than 5 % in all cases) the analytical system was found to respond linearly for all four compounds."

The respective statement in the main paper was modified to:



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"More details on instruments, linearity, identification and calibration can be found in the supplementary information."

Comment

p.4081, line 9 - The uncertainty on the C7F16 mixing ratio reported is around 5%. However, the calibration scale has an uncertainty of 15% due to the use of 85% n-isomer for the C7F16 calibration scale. This calibration uncertainty should be reflected in the reported mixing ratios.

Author response

The 15 % scale uncertainty of n-C7F16 is a calibration uncertainty and should not influence the detected trends and growth rates. It would produce unrealistically high error bars on both trends and growth rates if calibration uncertainties were to be added here.

Comments

Section 3.3 - Top-Down Emissions and Figures 8 and 9 - These errors on emissions seem rather high. Can the author explain how they were estimated? It would be interesting to run the top-down emissions through the 2-D model and see if the NH modelled mole fractions match the firn air results. Figure S3. The y-axis unit label should be [ppt/year].

Author response

As explained in the Figure caption "The short-dashed lines are uncertainty estimates consisting of a) the $1\sigma$ measurement standard deviations plus b) the square root of the sum of the squares of the of the deviation of the actual mixing ratios from the polynomials fitted to derive the growth rates plus c) an additional calibration scale uncertainty (see Supplement)." Here the calibration uncertainties have been considered as they could significantly alter the atmospheric burdens of these compounds. As for the 2-D modelling of the firn trend we note in section 3.1.1 that there are "considerable uncer-



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tainties connected with the firn reconstruction which do not allow further interpretation" and in section 3.1.2 "the limitations of the firn reconstruction which gives a smoothed view of reality, especially for reconstructions based on a single site with a limited number of data points in deep firn where age mixing is strong". Finally the y-axis in Figure S3 has been corrected.

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