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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric histories and growth trends of C_4F_{10}, C_5F_{12}, C_6F_{14}, C_7F_{16} and C_8F_{18}" *by* D. J. Ivy et al.

Anonymous Referee #1

Received and published: 13 February 2012

This is an interesting and pioneering study on some of the minor heavy weight PFCs with an impressive analytical achievement and long timeseries for both hemispheres. The paper is certainly worthy publication with its current content, however, it would have strengthened a lot by the inclusion of some emission estimates (even a simple 1-box approach and ignoring sinks would likely have allowed for the important comparison with the EDGAR bottom-up estimates).

Most of my comments are minor, perhaps with the only major comments being that the data should be published in numerical form, and Fig. 1 should be improved to better illustrate the discussed findings.

Abstract: The last sentence seems to be more a conclusion than a sentence of an abstract.

Introduction: For completion, I suggest to also mention the potential removal processes from the atmosphere (sinks).

p 4167, line 17: 'based top-down' should be 'based on top-down'

Experimental Methods:

Since the focus of this paper is on the measurements of these PFCs, a few experimental details should be clarified. Most of this could be done as supplementary material, if the author consider it too detailed for the general reader.

p. 4169, line 2: '50+'. Is this proper English, the 'plus' symbol is a mathematical operator and shouldn't be miss-used to abbreviate 'more than 50'.

p. 4169, line 4: Can you give a quantitative information on the blanks? It is not clear, if the blanks appear on both instruments, and of similar size for the two instruments.

p. 4169, line 7. Suggest to change 'three times the baseline noise' to 'three times the height of the baseline noise'.

p. 4169, line 15: 'A dry-air sample ...'. This is confusing, it implies that a CGAA sample was further dried and decanted into another tank. If so, mention, how the CGAA sample was dried, and why. The confusing part is that CGAA samples are not collected 'dry', and the use of the term 'dry-air'. Or maybe the authors simply wanted to say 'whole-air' instead of 'dry-air'?

p. 4169, line 23: This should probably be -79 C, not -97 C.

p. 4169, line 20: Could give some (semi-)quantitative estimates, on whether this zero air was free of these PFCs before the purification step, and whether this purification technique works to remove traces of PFCs from large amount of zero air, and whether the 'further purified' air was free of these PFCs? In essence, it would be valuable to know if the authors recommend this technique to remove these PFCs from (zero) air.

p. 4169, line 24: Can you give some information that would let the reader understand,

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what the lowest PFC concentrations in these dilution tanks were, if they were near detection limits, or if most of the measured samples' concentrations were within this measured linearity range. One could presumably calculate that from the 8 ppm CH4 and the dilution factors, but a brief statement in the paper would be better.

p. 4170, line 16. How many, how many per compounds?

p. 4171, line 10: 'dilution factor'. If the expressions 'enhancement factor', or 'enrichement factor' exist, these would probably be more appropriate that using the term 'dilution', as the spiking resulted in an enhancement, not a dilution.

p. 4171, line 14ff: These are presumably small peaks in ambient air. It would be helpful to mention the relative positions / retention times of these PFC compared to other well-known substances on these columns. When the mass spectra were determined using the spiked primary standards, did the relative signal sizes for the various PFCs agree with the signal strength sequence of published spectra?

4 Results and discussion

p. 4171, line 20: Does this scale have a name, e.g SIO-20xx? This would probably be the place to define one. Referencing these measurements to a scale with name will later help in the comparison with other measurements of the same or other groups on potentially different/evolving scales.

3 Archived Air Samples:

p. 4172, line 14 and line 24, and maybe elsewhere: Change 'Whalen' to 'Wahlen'!

p. 4173, line 13: Somewhere it should be specified how 'global averages' were calculated in this work. Presumably simply the average between the spline fitted NH and SH data (then perhaps the spline fitting should be explained first). Or have there been some corrections applied taking into account the latitudinal gradients within the NH as seen in many other anthropogenic trace compounds?

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p. 4173, line 14: 'decreases in inter-hemispheric gradients'. Given the lack of numerical data of the measurements and an inappropriate fig 1 scaling, such statements can unfortunately not be verified.

p. 4173, line 15–16, 'Emissions ...'. Is this a conclusion from the observations, or are the authors stating a finding from elsewhere, e.g the NH predominant emissions from EDGAR? This should be clarified, and if necessary, a reference to the literature should be added.

p. 4173, line 15: 'anthropogenic'. Based on this study, could you conclude concerning upper limits for potential natural PFC backgrounds/sources, Presumably for C6F14 and C7F16, you can exlude a natural background at the level of detection limit. It might be valuable to make a quantitative statements on this.

p. 4173, line 16, line 17: The expression 'Northern Hemisphere' is used despite earlier abbreviations (NH). Use in a consistent way. Looks like the same is true for 'Southern Hemisphere' and 'SH'.

p. 4173, line 21: Suggest to replace 'are' with 'were'.

p. 4173, line 26: '... higher detection limit(s) (there are two detection limits for this compound) ... Or it could be due to lower emissions, which should be mentioned explicitly.

p. 4174, line 9: Sentence confusing: '... and has been to shown to have ...'. Could you be more specific about 'non-background mole fractions' for the C2F6, C3F8, SF6, 'elevated mole fractions', or also 'depleted mole fractions'?

p. 4175, line 6. Maybe a reference is needed after 'C3F8' for this statement.

References: p. 4176, line 21: Change 'Izbick' to 'Izbicki'

Figures and Tables:

Please provide table(s) with numerical results of the measurements and a mentioning

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(maybe general) of the measurement precisions. These data should become publicly available, and the best place is right here in the paper (maybe in suppl materials).

Table 1. Could you explain why the lifetime numbers for some of the PFCs are in parentheses?

Figure 1: This figure is much too small, one can even hardly see the interhemispheric gradient. Improve by vertical spreading and / or separation in several figures. A few more tick marks and tick marks label would also greatly help to better interpret this figure.

Figure 1: C8F18: Spline fit through NH data. It seems that the (very unprecise) measurement of a single sample in about 1992 determines the entire NH evolution from about 1982 to 2000, and deviates strongly from the precise measurement in $\sim$1987. This fit would probably come out completely different without the 1992 result, and would match the older and younger observations much better.

Figure 2: Similar comment Fig. 1. Here the situation with the tick mark labels is even worse some subplots have only min and max ticks and labels.

Figure 2: For C6F14, there are a few years, where the SH growth rates are larger than any of the calculated NH growth rates in the entire record. Is this scenario possible, or is it a computational (uncertainty) artefact? If the NH is the driving force, it is hard to understand how the SH growth rates can ever be higher, shouldn't the NH growth signals 'dampened' as they propagate into the SH. C8F18 seems to show something similar. Similar comment on the SH growth rates onsets for C4F10 and C6F14, which are presumably also a computational artefact?

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 4165, 2012.

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