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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.

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We would like to thank the anonymous referee for their helpful and thorough comments. We have listed the referee's comments in italics and then written a response below each comment. We've additionally included text from the paper when it has been changed based on a comment.

Referee 1: *"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)."
Author Response: Thank you for the positive comment on our work. We have excluded emission estimates from this study as we are currently doing a detailed analysis of emission using a 3-dimensional model for a future paper. We hesitat to publish any numbers using a 1 box model, as the numbers will surely change in the subsequent study, possibly causing confusion to readers.

Referee 1: *"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."*
Author Response: We have replaced Figures 1 and 2 with 5 new figures (we have attached the figure C_4F_{10} to show the improved readability). The annual hemispheric mole fractions and growth rate based on the smoothed spline fits are now presented in Tables 3-7. Additionally, we have included the measurement data in the supplementary material.

Referee 1: *"Abstract: The last sentence seems to be more a conclusion than a sentence of an abstract."*
Author Response: We have removed the last sentence from the abstract.

Referee 1: *"Introduction: For completion, I suggest to also mention the potential removal processes from the atmosphere (sinks)."*
Author Response: We added a sentence discussing the sinks in the introduction and a citation for it.
"The main sink for the PFCs is photolysis by Lyman-α radiation and a minor destruction pathway is reaction with O(^{1}D) (Ravishankara et al., 1993)."

Referee 1: "p 4167, line 17: 'based top-down' should be 'based on top-down'"
Author Response: We added "top-down" to be an additional way to address these kinds of emission studies. We have included it in parentheses to help clarify.
"Both the aluminum and semiconductor industries have made efforts to reduce emissions of the lower molecular weight PFCs to the atmosphere, although global bottom-up inventories do not agree with atmospheric measurement based ("top-down") emission estimates (Mühle et al., 2010; International Aluminium Institute, 2011; Semiconductor Industry Association, 2001; World Semiconductor Council, 2005)."

Referee 1: "p. 4169, line 2: '50+'. Is this proper English, the 'plus' symbol is a mathematical operator and shouldn't be missused to abbreviate 'more than 50'."
Author Response: We changed the plus symbol to 'more than'.
"Additionally, only a select number of species were measured in this experiment to further improve sample precisions, as compared to the more than 50 species typically measured as part of the AGAGE network."

Referee 1: "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."
Author Response: We have added the blank values used in correcting the data for both instruments for C_6F_{14}, C_7F_{16} and C_8F_{18}.
"A small blank was detected for C_6F_{14}, C_7F_{16} and C_8F_{18} (0.008 and 0.005 ppt for C_6F_{14}, 0.012 and 0.013 ppt for C_7F_{16}, 0.017 and 0.016 ppt for C_8F_{18} on the CSIRO and SIO instruments, respectively), most likely due to the Nafion dryers used in the Medusa, and the observations were corrected accordingly."

Referee 1: "p. 4169, line 7. Suggest to change 'three times the baseline noise' to 'three times the height of the baseline noise'."

Author Response: We've added 'the height of'.
"The detection limits for each species on both instruments were estimated as three times the baseline height of the noise of the target ion immediately preceding and following the elution of the species and are presented in Table 2.".

Referee 1: "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'?"
Author Response: Thank you for the suggestion, we have changed 'dry-air' to 'whole-air'.

Referee 1: "p. 4169, line 23: This should probably be -79 C, not -97 C."
Author Response: Thank you for noticing. We have updated it to be -79C.

Referee 1: "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."
Author Response: We measured the zero-air and found it to be analyte free for these PFCs and have added a sentence about this.
"The zero-air was measured on the Medusa and found to be analyte free for the PFCs studied here."

Referee 1: *"p. 4169, line 24: Can you give some information that would let the reader understand, 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."*
Author Response: All of the subsamples were detectable for C_6F_{14}, and all but the lowest concentration subsample were above the detection limit for the rest of the PFCs. We have added a sentence to reflect this. As the archived air samples span the entire range (even below the detection limit), the dilution tanks cover most of the range of concentrations measured.
"All but the lowest concentration subsample of 6.25% were above the detection limit for C_4F_{10}, C_5F_{12}, C_4F_{16} and C_8F_{18}. The lowest concentration subsample was slightly above the detection limit for C_6F_{14}."

Referee 1: *"p. 4170, line 16. How many, how many per compounds?"*
Author Response: We made four primary standards for the scale and have updated the paper with this.
"Four primary standards were prepared at SIO to identify and quantify the heavy PFCs on the Medusa."

Referee 1: *"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."*
Author Response: We changed dilution to enhancement factor.
"The enhancement factor of the PFC/CFC-12/N_2O mixture added to the real air sample was determined by measuring the final CFC-12 mole fractions on the Medusa."

Referee 1: *"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?"
Author Response: We have added additional compounds and their retention times to Table 2. Additionally, we have compared the measured mass spectra with those available from the NIST database. The two agreed and we have added a sentence to reflect this.
"The mass spectra of the high molecular weight PFCs agree with published spectra from the National Institute of Standards and Technology and the retention times are consistent with what is expected based on their boiling points (NIST, 2011)."

Referee 1: *"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."*
Author Response: We've referenced the scale as SIO-2012. Thank you for the suggestion. "Four primary standards were prepared and the calibration scale, referred to as SIO-2012, has estimated accuracies of 6.8 % for C_4F_{10}, 7.8 % for C_5F_{12}, 4.0 % for C_6F_{14}, 6.6 % for C_7F_{16} and 7.9 % for C_8F_{18}."

Referee 1: *"p. 4172, line 14 and line 24, and maybe elsewhere: Change 'Whalen' to 'Wahlen'!"*
Author Response: Thank you for catching the typo - we have corrected it.

Referee 1: *"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?"
Author Response: We have rearranged the results to discuss the spline fits at the beginning and mention that the global averages are the mean of these values.
"Due to the sparseness of the available data set, the presented annual mean mole fractions and growth rates are based on cubic smoothed spline fits to the observations. The observations were weighted by their measurement uncertainty and a 50 % attenuation period of 4 years was used, which is slightly larger than the mean data-spacing, in estimating the smoothing splines (Enting et al., 2006). The uncertainties associated with the spline fits were estimated using a Monte Carlo approach using the measurement uncertainties associated with the observations. The smoothed spline fits are shown along with the observations in Figs. 1-5. The bottom panels of Figs. 1-5 show the annual hemispheric growth rates estimated from the cubic smoothed spline fit for each PFC. The uncertainties associated with the growth rates were also estimated as the 1-σ standard deviation from the spline fits estimated using the Monte Carlo approach. Additionally, the data are presented in numerical form in Tables 3-7."

Referee 1: *"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."*
Author Response: We've updated the figures and added the numerical data to Tables 3-7.

Referee 1: *"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."*
Author Response: We referenced EDGAR and hopefully made this clearer.

"Emissions of these high molecular weight PFCs based on EDGARv4.2 are of anthropogenic origin and primarily released in the NH (ER-JRC/PBL, 2009)."

Referee 1: *"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. "*
Author Response: Firn air samples showed no natural abundance for the PFCs studied here. We've added a sentence to reflect this.
"Analysis of firn air samples confirm that there is no natural abundance for these PFCs."

Referee 1: *"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'."*
Author Response: We updated 'Northern Hemisphere' with NH and same for the SH.

Referee 1: *"p. 4173, line 21: Suggest to replace 'are' with 'were'."*
Author Response: We have replaced are with were.

Referee 1: *"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.*
Author Response: Thank you for the suggestion. We believe it's due to lower emissions, as the detection limits for these compounds are nearly the same.
"C_8F_{18} follows a similar trend to that of C_6F_{14}, although it is not detectable until the mid-1990s, see Fig. 5, which is most likely due to lower emission rates."

Referee 1: *"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'?"*
Author Response: We updated non-background to depleted.
"There is one anomalous NH tank with a fill date in 1986 for C_6F_{14}, C_7F_{16} and C_8F_{18}, which has lower atmospheric mole fractions than the SH tanks with similar fill dates. However, this 1986 NH air sample is below the detection limit of the SIO instrument; additionally, the tank was not filled for the purpose of an air archive and has been to shown to have depleted mole fractions for C_2F_6, C_3F_8 and sulfur hexafluoride (SF_6) most likely due to the fill technique."

Referee 1: *"p. 4175, line 6. Maybe a reference is needed after 'C3F8' for this statement. "*
Author Response: We added the Muhle et al. (2010) reference.

Referee 1: *"References: p. 4176, line 21: Change 'Izbick' to 'Izbicki' "*
Author Response: Thank you for catching the typo - we have updated the reference.

Referee 1: *"Figures and Tables: Please provide table(s) with numerical results of the measurements and a mentioning (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)."*
Author Response: We've added the numerical results from the spline fits to Tables 3-7 and have added our measurements to the supplementary material.

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

Author Response: Those lifetimes have not been measured and are just an estimate. We added a footnote to the Table 1.
"*Lifetimes in parentheses have not been measured and are an estimate."

Referee 1: *"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."*
Author Response: We've updated the figures.

Referee 1: *"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 ?1987. This fit would probably come out completely different without the 1992 result, and would match the older and younger observations much better."*
Author Response: We have excluded the 1991 NH point in estimating the spline fit, although we have still show the observation in the figure.

Referee 1: *"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."*
Author Response: We've updated the figures.

Referee 1: *"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?"

Author Response: The higher maximum growth rate in the SH, as compared to the NH, is most likely a computational artifact due to the lack of NH measurements in the 1990s, when the growth rates are the highest. In general, the SH growth rates lag the NH rates, confirming that the majority of the emissions are in the NH. We have added a sentence to the Results discussing this.

"Additionally, the maximum growth rate is higher in the SH than in the NH for C_6F_{14} and C_8F_{18}. This is most likely a result of the lack of NH data in the 1990s to constrain the cubic smoothed spline fit and not that SH emissions dominate globally."

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

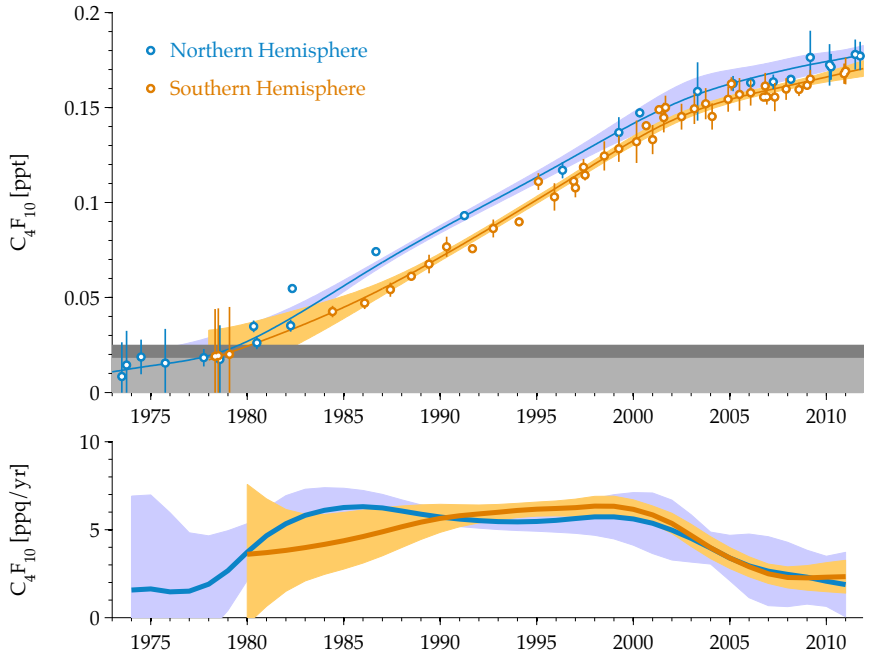

Fig. 1.