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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 one. We've additionally included text from the paper when it has been changed based on a comment.

Referee 2: *"This is a good paper reporting on a nice piece of work describing new atmospheric measurements of a number of perfluorinated carbon compounds. A good deal of the paper is appropriately dedicated to describing the details of these new measurements, however number of details could be improved and are described in the review below. There are also some minor points made in the results and discussion that don't appear to be supported by the data presented. I also find it surprising that*

rough estimates of global emissions aren't presented, especially since some of the discussion is dedicated to interpreting what the data suggest about emissions and how they have changed in the past. It would seem worthwhile to ask the authors why this information will appear only in a separate paper."

Author Response: Thank you for the positive comments. We are currently preparing a detailed analysis of emission estimates using a 3-dimensional global chemical transport model, which will be submitted in the next few months. We thought it best to separate the papers into an experimental one and a theory one, as there are so many compounds being presented at once. Due to the future work to be presented on emissions, we are hesitant to infer any emissions using a 1 box model, as surely our future paper will show discrepancies and may confuse readers.

Referee 2: *"On the abstract: Line 15,16,it seems quite unusual to report an average rate of increase over a 30+ yr period when that rate has changed substantially over time. . ."*

Author Response: We've changed this to just reflect the 2011 annual global average growth rates.

"The 2011 globally averaged mean atmospheric growth rates of these PFCs are subsequently lower at 2.12 ppq yr^{-1} for C_4F_{10}, 1.33 ppq yr^{-1} for C_5F_{12}, 4.96 ppq yr^{-1} for C_6F_{14}, 3.30 ppq yr^{-1} for C_7F_{16} and 0.93 ppq yr^{-1} for C_8F_{18}."

Referee 2: *"Line 15 of abstract and line 19 of conclusion. The contribution of these PFCs is estimated to be 0.35 mW/m2, and this is stated as being 3.6% of the total from all PFCs. This percentage seems too small considering the contributions of other PFCs shown in Figure 1-24 of Chapter 1 of the recent WMO ozone assessment and the fact that these other PFC contributions haven't increased all that rapidly in recent years."*

Author Response: We were including the natural abundance of CF_4 when we estimated

this lower percentage. We have used the WMO numbers and included the c-C_4F_8 mole fractions to calculate a 6% contribution to the total PFC anthropogenic forcing.
"These atmospheric mole fractions combine to contribute to a global average radiative forcing of 0.35 mW m^{-2}, which is 6 % of the total anthropogenic PFC radiative forcing (Montzka and Reimann, 2011; Oram et al., 2012)."

Referee 2: *"Last sentence of the abstract is unusual; it is not at all clear on what is being verified and why it is necessary."*
Author Response: We have removed the last sentence from the abstract.

Referee 2: *"On the main text and conclusion: p. 4172, line 21, could be clearer: is it true that the four archive samples that were also apparently contaminated were not sampled/stored in Al cylinders? Were they also stored in electropolished SS tanks?"*
Author Response: These tanks were stored in electropolished stainless steel tanks. Most likely this contamination is due to a local source at the station influencing the measurements. We have also updated this to include a 2002 tank that appears contaminated as well. We have added a sentence to clarify this.
"These five tanks were all stainless steel cylinders, therefore most likely a local source at the Cape Grim Station influenced these tanks."

Referee 2: *"p. 4173, line 10, 0.015 and 0.011 ppt for these two PFCs are below the detection limits reported in Table 2, hence it is unclear why the discussion is different for the C6 and C7 PFCs, where the paragraph starts off with the statement that these chemicals "are not detectable..."*
Author Response: We were hoping to mention that while C_4F_{10} and C_5F_{12} are technically below our estimated detection limit, they still are present in the earliest of samples. Hopefully we have made this clearer in the paper.
"C_4F_{10} and C_5F_{12} are present in the earliest archived samples at 0.015 ppt and

0.011 ppt respectively, but these measurements are considered below the estimated detection limits of the instruments, see Fig. 1 and Fig. 2."

Referee 2: *"p. 4173, line 16 and 17 and p. 4174, line 5. How is it that we know that the emissions of the C4 and C5 PFCs are primarily from the NH (a citation needs adding, or some short argument considering the uses needs to be made)?"*
Author Response: We have based this information off of the emission estimates from EDGARv4.2 and have added the EDGAR reference.
"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 2: *"p. 4173, line 19. Higher variability is not apparent in NH archive results, despite the assertion in the text. Residuals to the smoothed fits actually look like they could be larger in the SH record for some gases."*
Author Response: We have clarified this to reflect only for C_4F_{10} and C_5F_{12} in the early 1980s. Most likely the larger residuals for the SH spline fit is due to the higher frequency of data, as compared to the NH data, where the spline only has to fit a few data points and is more loosely constrained due to the selected spacing.
"Additionally, higher variability in the NH samples can be seen in the early years for C_4F_{10} and C_5F_{12}, as compared to the SH samples. This is attributed to sampling of less well mixed air due to emissions originating primarily in the NH, although efforts were made to fill the archive tanks during baseline conditions."

Referee 2: *"p. 4173, line 23 (also in abstract and discussion of radiative forcing), the term "globally averaged background tropospheric mole fraction" does not seem appropriate, given that this metric is derived from samples at two sites only. Some caveats need mentioning. . .and more accurate descriptions supplied. I imagine that the mean of the results from these two sites could provide a reasonable estimate of*

the globally averaged background mole fraction, but some discussion is warranted to ensure the reader understands that this is an extrapolation."
Author Response: We have rearranged the results so the description of the smoothing spline fit is presented earlier and have clarified that the globally averaged values are based on these spline fits. We have also added Tables that show the annual hemispheric mole fractions and growth rates calculated from the spline fits.
"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 2: *"p. 4174, lines 5 through 10, it doesn't seem likely that reduced mixing ratios for a trace gas arise from sampling non-background conditions..."*
Author Response: The referee is correct; most likely the reduced mixing ratios are due to the fill techniques used on these tanks. We have updated the paper with this idea.
"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 2: *"p. 4174, lines 25 through 27, why not include these growth rates in Table 3?"*
Author Response: We have removed Table 3 and replaced it with Tables 3-7, which show the hemispheric annual average mole fractions and growth rates estimated from the spline fits.

Referee 2: *"p. 4176, lines 1 through 5. Citations are needed that describe the efforts of industry to reduce emission. Also would be good to understand the relative emissive contributions of concerted use of these PFCs (ODS replacements) relative to unintended releases as a result of industrial manufacturing (Al production)."*
Author Response: There does not appear to be any unintended releases of these PFCs. Aluminum smelter samples were measured at CSIRO and did not show enhanced concentrations of these gases. I have removed the aluminum industry reference as it was confusing.
"Additionally, future observations of these high molecular weight PFCs will be important in confirming that the semiconductor industry, which primarily focus on the low molecular weight PFCs, are indeed reducing global PFC emissions (Semiconductor Industry Association, 2001; World Semiconductor Council, 2005)."

Referee 2: *"Terms that could be better defined: Optimized emissions First-in-kind emission"*
Author Response: We have replaced "optimized" with atmospheric measurement based and have elaborated on how this is a first-in-kind emission source.
"Moreover, C_5F_{12}-C_8F_{18} (liquids at room temperature), have a first-in-kind emission source for fluorinated compounds, where previously deionized water and a mixture of glycol and deionized water were used, from their use as heat transfer fluids in the semiconductor industry (UNEP Technology and Economic Assessment Panel, 1999;

Tsai, 2009)."

Referee 2: *"Items that would be more informative if quoted more quantitatively: p. 4169, line 4, "a small blank", about how large? line 21, I presume the diluent air was checked for PFC contaminant levels?"*
Author Response: The diluent air was checked for blanks and found to be free of these PFCs. We have added the blank correction values used to the text.
"The zero-air was measured on the Medusa and found to be analyte free for the PFCs studied here."
"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 2: *"p. 4170, line 13-14, what was the magnitude of this non-linearity parameter throughout the measurement range?"*
Author Response: The non-linearity parameters were relatively small. We have added the range of values of non-linearity parameters used.
"These nonlinearity parameters were relatively small and ranged from 0 to 0.048, with the largest nonlinearity correction for C_8F_{18}."

Referee 2: *"Table 2: define "standard precisions", is this the mean (median, 90%tile, ...) precision of repeat injections of a real air sample at ambient mole fractions, or a representation of the consistency in the prepared standards, or something else?"*
Author Response: We have added the footnote: 'Standard precisions refer to the 1-σ standard deviation taken on the working standard used, which is a NH 2010 tank.' to Table 2."

Referee 2: *"Table 3: I'm not convinced that the mean concentrations and growth rates during the period 1973-2011 are informative metrics to present to readers (see also my comment on the abstract). Certainly the 2011 metrics and rates for changes over recent years are informative and useful."*
Author Response: We have removed this table and included the annual hemispheric concentrations and growth rates for 1980 to 2011 based on the cubic smoothed spline fits in Table 3-7.

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