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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Perfluorocyclobutane (PFC-318, $c$-$C_4F_8$) in the global atmosphere" *by* Jens Mühle et al.

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We thank reviewer #2 for the very positive reviews and helpful suggestions. Below we repeat the comments, questions, and suggestions from reviewer #2 in italic and add our replies in bold. If we quote sentences from the manuscript, modified parts will be bold, while unmodified parts will not be bold. We have submitted revised main figures and revised Supplement text, figures, and tables as two PDF files in a zip file with our replies to reviewer #1.

**Reviewer 2:**



*The manuscript entitled "Perfluorocyclobutane (PFC-318, c-$C_4F_8$) in the global atmosphere" by Mühle et al. has been evaluated by this reviewer. The paper presents a substantial piece of measurement and modeling work on the atmospheric abundance and emission rates of perfluorobutane. The authors have developed an independent gravimetric c-$C_4F_8$ calibration scale and characterized the abundance of c-$C_4F_8$ with high precision in both hemispheres in order to determine historical emissions (archived samples) and recent global emissions. Using inversion modeling techniques, regional emission patterns (and pollution events) are investigated in detail, revealing that major c-$C_4F_8$ sources are found in heavily industrialized provinces of China (and perhaps Russia), due to the production of PTFE and other fluoropolymers. They predict c-$C_4F_8$ emissions will continue to rise and that c-$C_4F_8$ will become the second most important PFC emitted to the atmosphere in terms of CO2 equivalent emissions.*

*General Comments: The manuscript is a pleasure to read, has very few technical errors, and presents and an impressive amount of interesting data. The authors have done a commendable job to present a succinct and encompassing description of the methods and the results. The conclusions follow elegantly from the data presented and form a compelling narrative, especially considering the magnitude of difference in the potential emissions sources involved. I have only few scientific comments/questions. Those are listed below here, followed by technical (suggested) corrections:*

**We thank the reviewer for the very positive overall evaluation of our research article. We are very pleased that the reviewer agrees with our line of reasoning and conclusions.**

*Specific Comments:*

*L55: ": : :. explaining the increase in emissions." Presumably the authors here refer to the early/pre 1980's?*

**This indeed needed a clarification. We added "in the 1960s/70s" in the Abstract.**

*L65: "Significant emissions" must be inferred significant emissions?*

**Yes, this is correct as in the difference between global emissions and the sum of regional emissions. We changed as suggested by the reviewer to "**significant emissions **inferred" in the Abstract.**

*L115: What is "aerolyzed foods"? Please explain (very briefly), or used more common term.*

**We thank the reviewer for pointing out this mistake in the Introduction. We meant aerosolyzed foods which refers to foamed food products and sprayed food products, but this is perhaps not very commonly used. Therefore, we have replaced this with "foamed/sprayed** foods**".**

*L262: Please explain what is meant by "above bubble close-off".*

**Throughout the firn (compacted snow), air is contained in tiny channels that are open to the atmosphere. As more snow accumulates at the surface, the weight of the snow above causes the channels to be compressed and they eventually close to form discrete bubbles of air embedded in ice. Below this point the air cannot be pumped out anymore. We have modified the sentence in third paragraph in Section 2.3 to "**... from 19 depth levels in the firn from **the** surface to **80.06 m (below this depth firn air can no longer be collected as the open channels in the firn have closed off and formed discrete air bubbles embedded in ice)."**

*L396-397: "it was assumed that emissions were constant from year to year". This*



*seems confusing to me. Perhaps I'm not understanding this inversion correctly. I can see that the emissions would be assumed constant during the year, but why from year to year? How does this work?*

**We agree that this sentence at the beginning of Section 4.3.2 could be better worded. When a Bayesian inversion is performed, certain "a priori" assumptions need to be made to inform the inversion. These are often times emissions from a bottom-up inventory, which are believed to be reasonably close to reality, but bottom-up emissions for *c*-$C_4F_8$ are significantly too low. Therefore our approach, which has been used extensively in the literature, was to assume that emissions in any given year are similar to the previous and the next year, but to allow for a certain change (year-to-year emissions growth), that is we expect emissions to only change gradually. We rephrased the sentence to "**A priori, it was assumed that emissions were **similar** from year to year **such that** the ***a priori*** year-to-year **emissions** growth rate **was assumed to be zero with an uncertainty** of 200 t yr$^{-2}$ (0.2 Gg yr$^{-2}$, **1**$\sigma$), approximately twice the bottom-up estimate in Sect. 3.**". Note, that we also corrected the unit from t yr$^{-1}$ to t yr$^{-2}$ (Gg yr$^{-1}$ to Gg yr$^{-2}$), as it is an uncertainty in the emissions growth rate, and specified that it is a 1$\sigma$ uncertainty.**

*L440: "We do not report emission estimates outside of eastern Asia due to large posterior uncertainties but include them assisted with determination of the boundary conditions". I do not understand this approach. Please clarify and explain.*

**We agree that this sentence in the third paragraph of Section 4.4 was rather confusing. Emission estimates far from the measurement station will be highly uncertain, both in terms of their spatial distribution and magnitude. We therefore choose to only report emissions for a region where the uncertainty is small enough that we are able to draw conclusions from the estimates, here eastern Asia. Nevertheless, the emissions outside of the reported region are still esti-**

**mated in the inversion as they may contribute to pollution events measured at GSN. The contribution to the absolute error to the modelled mole fraction from distant emissions sources is small, but the resultant uncertainty in their inferred emissions is large. This leads to larger uncertainty in the reported regional emissions if they are included, which may hinder interpretation of results. To clarify, we changed to sentence to "W**hile w**e do not report emission estimates outside of eastern Asia due to large posterior uncertainties, **they are still estimated in the inversion as they are useful when modelling emissions in eastern Asia and their uncertainties that we do report.".**

*L538: Please explain why not incorporating the firn data has this impact on the emissions estimates.*

**Prior to 1980, the Bristol inversion is based on sparse, uncertain NH archive data, and the CSIRO inversion on the same NH archive data plus firn data with age distributions covering roughly 40 years. The differences between the inversions before the early 1980s are within the estimated uncertainties for these reconstructions as can be seen in Fig. 5. We modified the sentence at the beginning of Section 5.2 to "**The Bristol inversion initially reconstructs lower emissions, but **the differences are within the estimated uncertainties for the reconstructed histories (see Fig. 5).".**

*L547: How can the mole fractions of this very unreactive compound change in the tanks?*

**The ratio of NIES/AGAGE *c*-$C_4F_8$ calibration assignments for two tanks exchanged between NIES and AGAGE (SIO) changed by more than 10% between**



**2008 and 2016, which is completely unacceptable. On the contrary, the IN/OUT values assigned by AGAGE (at the beginning and end of each tank's service time), agree for both tanks within precisions of 0.02 ppt ($\sim$1.1 to 1.7%). Therefore, we concluded that there must have been an internal calibration drift problem at NIES for *c*-$C_4F_8$ in tanks NIES used to assign calibrations to the two tanks exchanged with AGAGE/SIO. Unfortunately, we do not have enough data to characterize this further. One possible explanation for the drift (change of concentration) of such an inert perfluorinated compound could be the presence of Christo-Lube MCG111, which had been used by the manufacturer on a limited number of Essex tanks to deal with leak problems at the valve flange. MCG111 is a mixture of perfluorinated polyether (PFPE) and polytetrafluoroethylene (PTFE). We showed, without a doubt, that it is able to produce polyfluorinated compounds including *c*-$C_4F_8$ and $CF_4$ at ppt level, which caused a good deal of grieve for the AGAGE network. We still think that the sentence in the manuscript describes what the likely cause is, even though we did not include any of the details for brevity sake as we did not use the data. We slightly modified this and the previous sentence in the second paragraph of Section 5.2.**

*L553: $C_2F_6$ is here listed as a minor PFC, however in L122, it was a major. Which are the majors and the minors?*

**We agree that this is not consistent. In terms of mixing ratios, there is only one major PFC, $CF_4$, currently at $\sim$86 ppt in the Northern Hemisphere, while the other three PFCs could all be called minor PFCs with $C_2F_6$ at $\sim$4.9 ppt, *c*-$C_4F_8$ at $\sim$1.8 ppt, and $C_3F_8$ at $\sim$0.69 ppt. In terms of $GWP_{100}$ $CO_2$ equivalent emissions, see old Fig. S8/new Fig. S9, $CF_4$ is also in its own league, while $C_2F_6$ and *c*-$C_4F_8$ $CO_2$-eq. emissions are similar but smaller and $C_3F_8$ $CO_2$-eq. emissions are even smaller. Therefore, we modified the sentence on L122 (Introduction) to "**While the major atmospheric **PFC**, tetrafluoromethane ($CF_4$) **as well as the minor PFCs**

hexafluoroethane ($C_2F_6$) and octafluoropropane ($C_3F_8$) are ... **". The use of "minor" in the two statements is now consistent with each other (last sentence of Section 5.2 and seventh paragraph of the Introduction).**

*L558: To make clear what we are talking about, I suggest inserting "from a climate forcing standpoint" before "will become the second most important PFC: : :".*

**We chose to modify the sentence at the end of Section 5.2 to: "***c*-$C_4F_8$ **$CO_2$-eq.** emissions have been ..., so that *c*-$C_4F_8$ will become the second most important PFC emitted into the global atmosphere **in terms of $CO_2$-eq. emissions."**

*"Technical" Comments:*

*L42-43: The propagated uncertainties on the emissions should be given in the abstract.*

**Agreed. We added 1$\sigma$ uncertainties to the Abstract: "**... the 1960s to 1.2 $\pm$ **0.1 (1$\sigma$)** Gg yr$^{-1}$ in the late 1970s to late 1980s, then declined to **0.77** $\pm$ **0.03** Gg yr$^{-1}$ in the mid-1990s to early 2000s, ... rise since the early 2000s to 2.2**0** $\pm$ **0.05** Gg yr$^{-1}$ in 2017**". We changed this accordingly in the "Summary and Conclusions" section.**

*L61: " in agreement with our analysis". This seems like an obvious statement. Suggest deleting.*

**Agreed. We deleted it from the Abstract. We also deleted this in the "Summary and Conclusions" section.**

*L102: "Recently there is also further evidence: : :". This sentence begins awkwardly –*



*suggest rewording it.*

**We changed the sentence in the Introduction to "Today we also have** further evidence that ... **".**

*L249: "Fig.1." Other places in the manuscript "Figure" is used. Check for consistency.*

**Our understanding is that ACP requires the use of "Figure" when it stands at the beginning of a sentence and "Fig." when it stands anywhere else in a sentence.**

*L302: Perhaps "default" is a better word in place of "definition".*

**We agree that "by definition" was not the right choice of words, but "by default" does not seem right either. We modified the sentence in Section 3 to "However, t**hese data are **inherently** not representative of total global emissions **since** developing countries do not... **".**

*L311: Move the definition of 1t =0001Gg to the introduction paragraph, where Gg is first used.*

**Done. We moved this to the Introduction.**

*L316: replace "similar to" with "analogous to what has been observed for".*

**Done. We also modified the beginning of the sentence in Section 3: "As** ha**s** been **found** by Saito et al. (2010) and Oram et al. (2012), we show in Sect. 5.2 and 5.3 that measurement based ("top-down") global and most regional emissions are significantly larger than the compiled bottom-up ***c*-$C_4F_8$ emissions** inventory information (see Fig. 5), **analogous to what has been found for** other PFCs (Mühle et al., 2010), reflecting

the shortcomings of current emission reporting requirements and inventories".

*L641: Insert "occurring" before ": : :in China: : :)*

**Done (last sentence in Section 5.3.1).**

*Line 689-691: These two sentences belong more appropriately in sections 5.35 and 5.3.6.*

**On one hand, we agree with the reviewer. On the other hand, these two sentences at the end of Section 5.3.4 serve as transition from 5.3.4 to 5.3.5 and 5.3.6. Moreover, the first sentence applies to both 5.3.5 and 5.3.6 and would have to be repeated if moved. Unless the reviewer feels strongly about this, we prefer to leave it as is.**

*Figures:*

*Figures 1 is nicely formatted, but the formatting is inconsistent with that applied in Figures 2-4. Moreover Figure 5 has a completely different formatting style. This figure formatting ought to be "harmonized".*

**For Fig. 1, we increased the fonts sizes and stroke of the box and tick marks (it was also updated following reviewer #1's request to add interhemispheric gradient and confidence bands). For Fig. 5, we adjusted the fonts, changed the color of the box and tick marks, added an axis at the right and top, and removed the outer box. Both Figures now more closely resemble Figures 2 – 4. We hope that no further changes will be needed.**



*Figure 1 caption: What are the error bars?*

We added to the figure caption "**For individual samples, error bars reflect measurement precisions. For monthly means, error bars represent standard deviations.**"

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