

***Interactive comment on* “Trends and Emissions of Six Perfluorocarbons in the Northern and Southern Hemisphere” by Elise S. Droste et al.**

Anonymous Referee #1

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In this study, Droste et al present improved analytical capabilities to separate isomer of long-lived perfluorocarbons (PFCs). A few years of updated measurements of PFCs from three sample sets are given and complemented with older published work. Global emissions are derived and compared to inventory-based and earlier observation-based emissions estimates. The work presents some important advancements in analytical techniques and important long-term observations and emissions estimates. Source regions and source types are also discussed here. The manuscript is generally well written and understandable.

My major comments are on some clarifications related to primary calibration, more quantitative comparison to recent work by Laube et al, the publishing on the actual measurement results, and Figure improvements. These are interspersed into the gen-

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eral comments below.

Abstract, p. 1, l. 5: Perhaps add 'analytically', to clarify what 'separation' is discussed here (analytically separated from their isomers ...)

p. 2, l. 4: is 'metric' necessary (isn't ACP using SI units anyway?).

p. 2, l. 6 'despite what?', what does 'this' reference to?

p. 2, l. 5: Does the two-thirds refer to the emissions of the last 8 years or to the emissions since 1978?

p. 3, l. 18: is decofluorobutane. Spelling here different to abstract

p. 3, l. 19: hexodecafluoroheptane. Spelling here different to abstract.

p. 3, l. 21: same issue for perfluoro-2-methylpentane. Suggest to recheck spelling of all chemicals and use consistently throughout.

p. 3, l. 24. '... of these...' would strictly refer to c-C4F8 and n-C5F12, but I presume that the author means all compounds handled in this manuscript.

p. 3, l. 24. In Table 1, there is a compound with a GWP outside the range indicated here (i-C6F14).

p. 4 objective 2: There is something fundamentally unclear here. Why were new calibration scales needed? I understand that with new methods, isomers could now be separated. However, were the old calibration scales not made with pure reagents, e.g pure n-C4F10, no i-C4F10? If so, then why weren't the old calibration reference standards used for the present work, and the air sample data corrected for the fact that now the two isomers are separated? It appears that the old calibration reference standards would still be good, but the measurement of the air samples would need to be redone or the old ones corrected. Was the same raw material used to produce the new scales. How many cali-bration reference standards were produced — just one?

p. 5, l. 14 – 16. It seems that this was already explained in the Intro objective 1.

p. 6, l. 7: Were compounds used in this study also affected? If not, perhaps be more specific by saying ‘..number of compounds not used in this study’.

p. 7, second para. Comment here is similar to p. 4, objective 2.: ‘..from the observe isomer’ observed where – in the old primary calibration standards? If there was i-C4F10 in the old standards, why wasn’t it precisely quantified by measuring it vs the new cal standards, then allowing to separate the <2.8% difference into the two factors ‘leak-tightness’ and ‘i-C4F10’ influence. Line 9. Lack of observed iso-mers where?

P. 7 l. 12: ‘The confidence in the complete separation of all isomers for C6F14 and C7F16 ...’ This sen-tence is in conflict with earlier mentioning of inabilities of separat-ing all isomers of e.g. C7F16.

p. 7, l. 19: ‘... did not differ significantly...’ seems incorrect, According to Fig. S2 they differ very strongly and significantly and are rather concerning.

p. 7, l. 27. The abbreviation does not seem to match the first letters of the full name.

p. 7, l. 30: Could you provide a guess why there is a difference between the boot-strapped CFC-11 and that measured on the NOAA scale. There is a lot of plural men-tioning, but isn’t it only one compari-son, that of the (single) working tank vs the primary calibration tanks?

p. 7, l. 31. How can an accuracy be negative (-5.5%).

p. 7, l. 31: It is incorrect to say that the improvement by the new calibration scale is significant. The improvement is max 2.8% as stated earlier. What improved a lot are the measurement results of the field samples, because i-C4F10 is now excluded from the n-C4F10 measurements. Again, this is mainly a correction of older air measurements, not an improvement of a scale.

p. 7, l. 34: How did you get to the 20% and 11%. Perhaps explain in more detail in

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the supplement. Labeling a calibration scale 'new' calls for problems down the road. It would be much clearer to give it a name.

p. 8, l. 4: 'horizontal'. Shouldn't this be 'vertical'?

p. 8, l. 7: Why would a 'not fully represented' atmospheric layer justify leaving it out, there is a good part of the stratosphere in the model.

p. 10, l. 10: Provide some more intercomparison for the c-C4F8 mixing ratio of this study and that of Muhle et al., 2019, either here or in the supplement. Add the Muhle et al. CGAA mixing ratio to the present results. Are the deviations a constant ratio or are there potential nonlinearity issues. Can you derive a calibration scale factor between the UEA and the SIO scales, perhaps based on the CGAA re-sults, or other ways of intercomparisons (Tacolneston?). A well-derived conversion factor is extremely useful e.g. for users of the many data sets presented here and in Muhle et al.

p. 12, l. 12. 'smaller elevations' Relative or absolute, or both?

p. 12, l. 22 and 25. The mentioning of the chemical formula in the parentheses is not necessary as al-ready introduced earlier on p. 4.

p. 13, l. 14. 'Mixing ratios in Taiwan . . . ' for which years?

p. 16, l. 34: Can you rule out that EDGAR has taken some emission results from Laube et al., 2012 to feed into their calculations and output? There are rumors that EDGAR is not always strictly taking in-ventory emission estimates. It might be worth to ask. Similar question for EDGAR and Ivy results (n-C7F16).

p. 17, l. 17. Please rephrase second part of that sentence, it is difficult to understand. Also the com-ment in parentheses (our calibration changed by 11%) appears odd, it does not seem to be the cali-bration that changed much, but the measured air samples changed a lot due to the fact that separa-tion is now possible.

p. 18, l. 1: eliminate one of the 'with'

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p. 18, l. 28. How can cumulative emissions represent a percentage increase? Please rephrase. Publish the measurement results in the supplement, preferably, in tables/files that are easy to down-load and use for future users. Clearly state, which calibration scale the individual data sets are report-ed on.

Table 1, footnote a). State somehow that the assumption made on lifetime is one made in the present work, and not in Myhre et al.

Table 4: What are the analytical precisions of the calibrations exactly? Is there a reason they are given as ranges, and not as mean value? It is difficult to understand for several reason, one because there is not a clear mentioning of how many primary calibration standards are made, if and how these are propagated (to what) and how many working standards are used. Also, mixing ratios in the primary calibration mixtures should be given. Explain 'accuracy for CFC-11' more in detail. Why isn't this simply a deviation (ratio) between the UEA primary calibration CFC-11 and that of NOAA? Again, why ranges? Also, ranges are given in an inconsistent way, sometimes from a small number to a large number (-1.4 to 2.8) and sometimes from a large number to a small number (-1.78 to -5.47). Footnote a) I don't understand the second part of the sentence (by calibrating pure compounds). I don't understand footnote b), please rephrase.

Figure 2: Contribution of what? Spelling mistake in legend (Cenral China)

Figure 5. It is very difficult to quickly get a good overview on this plot. The comment on the second-ary axis does not help much to directly understand, which of the two axes belongs to which com-pound. Suggest to extend '(blue circles)' by '(blue circles, left axis)', and correspondingly for '(green circles)', and then delete the sentence 'Note that ...'. Also, it would help a lot of the upper three sym-bols and descriptions would correspond to the upper part of the plot, i.e. suggest to put the three i-C6F14 legend entries on top (the current reversed way is the part that confuses most in this plot) (see Fig 4 where this is done correctly). Or split the legend in two. It would help to color-code the axis number and labels according to the plot colors. Lastly, it would also

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help if the left axis numbers stopped at the maximum values of the concentrations, i.e. at around 0.08 ppt. The sentence 'Data pri-or to 2010 ' is incorrect, there are open circles up to about 2013. There is either no light blue or no dark blue shaded area visible on this plot. The symbol plot colors are difficult to distinguish and in some cases of similar tone for the two different compounds. The legend symbol size should be made larger (on a printed copy, they can hardly be distinguished in their colors). Suggest to set the left x axis limit somewhat prior to 1978 to show the 1978 results in full (there seems to be one green circle at 1978. No blue circle?). Space required before '[ppt]' for n-C6F14 for both main and inset axis. Some of these comments apply to some of the other figures.

Fig. 7: Add the Muhle et al. 2019 emission results to this graph. Fig 7 – 9: Colors are difficult to distinguish. Use methods to better distinguish the various lines. E.g. in Fig. 7, the Oram et al. results aren't visible for most of the record.

References: p. 24, l. 18: capitalize 'US'.

Fig. S1. Section reference missing (currently ??).

Fig. S2. Line 2. 'samples collected after 2005'? or 'Samples measured after 2005'? Why? There is a large difference between the ion ratios for the calibration standard and the tank samples, why? This large difference implies that there is still some kind of a co-elution on the column used in the present work. Perhaps an integration problem? Mention here or elsewhere in the text, what mixing ratios the 'new' calibration standard has, and perhaps here, what the differences in peak sizes are typically for the CGAA samples and for the cal standard.. Also, for some compounds, the ion ratio of the 'old' Laube 2012 calibration scales could be added to here.

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