

Interactive comment on “Continued increase of CFC-113a (CCl₃CF₃) mixing ratios in the global atmosphere: emissions, occurrence and potential sources” by Karina E. Adcock et al.

Anonymous Referee #1

Received and published: 15 December 2017

Review for Adcock et al., Continued increase of CFC-113a (CCl₃CF₃) mixing ratios in the global atmosphere: emissions, occurrence and potential sources

The authors provide updated data sets for CFC-113a from various observation platforms and use these to update global abundances and emissions. These show that after a rapid increase in CFC-113a emissions in approximately 2010, they have now leveled off. Interhemispheric gradients and pollution events at the Asian stations are presented. Potential sources of CFC-113a are discussed, which however remain speculative.

The paper is an informative and useful update on a compound, little is known about.

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This study adds to other recent studies of newly-discovered compounds with no purposeful end use, and shows the necessity to distinguish the two isomers in order to de-tangle their stories. The paper is well written and understandable, but could benefit from some consolidating of information, in particular in the sections where the potential sources are discussed. The topic is well researched and the authors have done a good job in bringing the many data sets together. The supplement adds more information and data are made available. This paper is well suited for publication in ACP and I have only minor comments, which, once thoroughly handled, should make this acceptable for publication.

Introduction: A brief discussion on the loss mechanisms of CFC-113a would be helpful to understand the cycling of this compound through the atmosphere, in particular for the discussion on CFC-113a in the stratosphere.

p. 2, l. 77: What kind of pumps were used for the various sampling sites?

p. 2, l. 84: Please elaborate more on the use of different methods (chromatography columns) particularly to give insight which samples / batches of samples were measured one way or the other.

p. 2, l. 86: Primary calibration scale: Describe, or refer to the literature, on how the primary reference material was produced (how many primary standards, at what ppt level), and what the estimated accuracy is. Was the CFC-113a pure or contaminated with CFC-113? Accuracy of the NOAA calibration scale for CFC-113.

p. 2, l. 89: How did the repeated standard measurements feed into the calculation? Were these referenced against other standards, or were chromatographic peak sizes assumed constant over a day? How many standards were measured per day?

p. 2, Methods. If not published previously, please provide a few more analytical details. How well do CFC-113 and CFC-113a separate on the two columns used, which fragments were measured? If available, provide a spectrum of CFC-113a; how well

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does it compare with one from the literature?. If some ions were used for both isomers, what were their sensitivities if scaled to the same mole fraction on the MS used for this study? Does 'pure' CFC-113 normally have CFC-113a impurities or vice versa? Provide any other information that can be useful for comparison with other networks, which may not be able to separate the two isomers (this could all be in the supplement).

p. 3, l. 95: How many CGAA samples were added, were these equally spaces over the 2012 – 2017 period. Were some of the earlier samples from Laube et al., 2014 re-analyzed and if so, how did these agree with the present study?

p. 3, l. 109: Which is day and which is month in the xx/zz/yyyy date description. This can be rather confusing (and seems to be reversed in the supplementary tables), why not spell out the month(s), like e.g. p. 7 l. 290? This confusing style re-appears throughout the document.

p. 3, l. 124: The very first mentioning of CFC-113 here without any prior motivation for this leaves the reader confused.

p. 3, l. 125: Even though explained in details in the cited references, please provide a couple of sentences describing this model. Are the emissions derived from an inversion, was a prior used?

p. 3, l. 127: What is the UEA Air Archive?

p. 3, l. 126: Have the CFC-113 mixing ratios been published previously, or are these measurements part of the present study? By reading this sentence it is not a priori clear if AFEAS has also provided bottom-up emissions for CFC-113a.

p. 3, l. 131: What do the authors mean by 'isolated'?

p. 3, l. 138: Please explain why Tacolneston can be considered of NH background air given that there is apparently a gradient of CFC-113a in the NH. The absence of pollution events at Tacolneston may make this site representative for background air at that latitude at most. See similar issue p. 6 l. 268. 'Spikes' is a rather confusing term.

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p. 4, l. 141. I am not convinced about the shift to more southerly latitudes. Is this an assumption that was made, or a result of the model? If the former, on what basis is this assumption founded? If the latter, how can a model using Cape Grim data give such detailed results about the NH distribution, particularly when apparently Cape Grim is insensitive to the NH distribution as stated on p. 3, l. 133? The mentioning of Tacolneston observations here is confusing also, how could these be used to determine the NH latitudinal distribution over decades if there are only a few years of measurements? Also the comparison to Taiwan seems inappropriate if the authors use median values for that site rather than a 'Taiwan background'. Overall there seem to be too many degrees of freedom here to be able to pin-point such a detailed evolution of NH latitudinal gradients.

p. 4, l. 171 (Overall . . .) Is this sentence necessary?

p. 4, l. 176: Is the 0.03 ppt/yr increase a result of the model or some other kind of fit? The mentioning of 0.06 ppt/yr for Taiwan is somewhat misleading as it makes the reader believe that mixing ratios have grown more rapidly there, but isn't the Taiwan growth most likely tagged with a large uncertainty given the fact that the authors take the median values rather than deriving a real 'background' record for Taiwan.

p. 4 l. 182: The presentation of the result would evolve less confusing if the emissions were first mentioned before rates of growth of these emissions are discussed. Also, the mentioning of an average of 1.7 Gg/yr does not say anything about the variability of the emissions in these years (There is not a single mentioning of emissions for a specific year). It would be helpful to learn how much they varied in these years, by e.g. giving the range of emission for these few years. I presume that the numbers in parentheses are some uncertainty ranges, or are these the ranges they vary over that time?

p. 5, l. 185: Can this 2% offset (using the same primary calibration scale) be related that perhaps NOAA measures the combined CFC-113a/CFC-113 isomers? Also, there does not seem to be a description anywhere on how the NOAA scale for CFC-113 was

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adopted, and what the propagation uncertainties of this procedures might be. Which way is the offset, which network reports higher values?

p. 5, l. 200: It would be very informative to see a graphical comparison of the emissions for the two compounds over the last years, for example by adding those of CFC-113 to Fig 3, or to somewhere plot the ratio of the CFC-113a/CFC-113 emissions.

p. 5, l. 211: This is confusing, if the AFEAS data are used as the CFC-113 emissions in the model, then the sentence that follows does not make sense. Do the authors perhaps mean that the modeled emissions agree closely with the AFEAS bottom-up emissions?

Fig. 4: colors are very hard to distinguish, for example, colors for NOAA and modelled mixing ratios seem the same. Also, filled circles don't appear as such due to their close proximities. Dashed lines appear as dash-dotted in the legend. The matching of modeled and AFEAS data is perplexing – are AFEAS data used as prior? In which year does AFEAS end, 2000; it is not possible to see this on the graph? I see only one green Rigby uncertainty line. Are the uncertainties shown for the present study based on the 'likely' or 'possible' range (p. 5 l. 22) or something else?.

p. 5, l. 221: Lifetime work was really done by SPARC, it might be better to cite that work.

p. 5, l. 234: Do you mean 'related to CFC-113 emissions from (old) banks, i.e impurities of CFC-113a in CFC-113? This would not agree with their historic emission ratios. Please clarify.

p. 6, l. 243: I suggest to phrase the other way: When there are spikes, then the NAME model . . .

p. 6, l. 252: Were compounds other than those listed in Table 2 also looked at?

p. 6, l. 277: 'generally': Does this mean that this was not always the case and that some Cape Grim results were higher than Tacolneston. From Fig 5 inset, it is not easy

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to see this. Is the dark filled circle at the beginning of 2016 at ~0.75 ppt from Cape Grim (with uncertainties smaller than the plotting symbol)? l. 279: replace 'higher' by 'lower'.

p. 7, l 289: It is unclear, if only the three surface samples were used here for the inter-hemispheric comparison, or a historic reconstruction of the NH based on more samples. If only the surface samples were use, the mentioning of 'trend' is not adequate. Also, Greenland firn air samples are here declared as 'representative of background Northern Hemisphere CFC-113a mixing ratio', which (similar to the same statement for Tacolneston) seems to be in contradiction to the assumption of latitudinal gradients in the NH. The samples are hard to see in Fig. 5, perhaps but a year in the legend for 'Greenland (surface)'.

p. 7, l. 319: What is the 's' in parentheses?

p. 8, l. 334: I disagree with the statement on l. 333 ff, that the absence of a correlation is not what we would expect. Before, the authors rightly state, that the correlation between CFC-113 and CFC-113a may derive from co-located factories (this is a rather likely scenario, as there are large centers of industrial activities in China). Taiwan may simply see air from places where CFC-113 and CFC-113a factories are not co-located,

p. 8, l. 347: I am having difficulties to derive from Manzer 1990, that the CFC-113a route is a main pathway. It appears that he showed many pathways graphically, and listed two examples of potential pathways, neither of which was via CFC-113a. In contrast, Maranion et al., seem to suggest this route, but without backing it up with literature.

References: Laube et al., 2014: Captial 'A' For Brenninkmeijer, C. A. M.; Manzer, 1990. Reverse initials; Rigby et al., 2013: Correct Muhle

Fig. 2: Limiting the y axes labels to the range of the data would greatly help in distinguishing the two data sets. Are these error bars now also including some uncertainties

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of the standard measurements, as indicated in the main text?

Fig. 3: Similar comment as for Fig 2 for the right y-axis: Label ticks only in range where data are. For the mean emissions, a solid line rather than a dashed line would help to see the apex better. Date 04/12/2012 not apriori clear, which is month and which is day. Legend shows light blue filled circles but these can't be seen in the plot. Suggest to replace these by lines for the model results.

Consider to somehow show the CFC-113 emissions for the last decades in a different form, such that they could be compared to the CFC-113a emissions in Fig. 3 (perhaps add them there).

Fig. 5: It is very difficult to distinguish the various sampling sets. Please improve figure.

Fig. 7: There seem to be no error bars on the CFC-113a measurements.

Fig. 8: Why was this particular measurement chosen? There seem to be many elevated CFC-113a shown in Fig. 5.

SI Tables: Emissions are calculated for 2017 based on 2 samples only for Jan and Feb 2017. This is almost certainly biased and I suggest to omit presenting model results for 2017.

Consider complementing tables with informations on calibration scales used for the various compounds and data sets.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-978>, 2017.