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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Tropospheric observations of CFC-114 and CFC-114a with a focus on long-term trends and emissions" *by* Johannes C. Laube et al.

Anonymous Referee #2

Received and published: 5 September 2016

The focus of this paper is the isomeric pair CFC-114 and CFC-114 of these long-lived potent ozone-depletion compounds, which have been regulated by the Montreal Protocol. Samples of firn air and the Cape Grim Air Archive are analyzed for this study, many of which have been analyzed earlier on somewhat different instrumentation. The measurement results are used in combination with a 2-D model to reconstruct atmospheric histories of these compounds, and to assess their global emissions. The data sets are complemented by those from measurement campaigns in Taiwan and from CARIBIC. A focus of the manuscript is put on the relative abundances and emissions of the two isomers, for which the authors find a varying ratio over time.

This study is very well designed and carried out, delivering solid data sets and an dis-

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Discussion paper

tinction into the two isomers. The study is important in several aspects, it allows for a reconstruction of the CFC-114/a histories and emissions including most recent dates and highlights the importance of this so-far rather 'neglected' CFC. The separation into the two isomers reveals some additional new information and presents some new puzzles over the finding of a variable ratio of the emissions and the finding of preferential regional emissions of the CFC-114a over CFC-114. The manuscript is also well written. I have no objections to the scientific interpretation and discussion. I recommend publication after minor revisions.

Comments:

My only major comment is at the very end: publish the numerical results in the Supplements.

page 2, line 28: CFC-114a used in HFC-134a production: Could the authors (here or when discussing the Taiwan results) provide information (perhaps through the later-mentioned contact at DuPont) on the various production pathways for HFC-134a, which is currently the dominant production method, where (geographically) is HFC-134a produced (presumably mainly China?). These comments apply to here or page 9, line 29 (which pathway is dominant?).

page 3, line 13, this paragraph should be revised as it is somewhat unclear and confusing: Shouldn't Oram (1999) be mentioned here as one of the previous studies on CFC-114/CFC-114a — what did Oram (1999) find out related to the two compounds? Not having access to Lee (1994), p. 3, line 18, it is not clear, if Lee (1994) made measurements of these compounds or if that thesis dealt only with some calibration scales for the compounds under discussion.

line 17 ff. The sentence implies that 'the data compared' were Cape Grim measurements, but wouldn't these be the same data in both cases, those published by Oram (1999) except that i.e. Sturrock et al., 2002 used CFC-114 + CFC-114a while those from UEA (also Oram 1999) separated the two compounds. It would be missleading to

call this a 'pure' calibration difference.

page 3, line 28, line 30: Years should be in parenthesis, check entire manuscript for this deficiency.

section 3.2, Analytical technique: could you provide information on potential differences of the molar sensitivities of the two compounds for the two measured mass fragments. Are e.g. for mass 134.96, the peak heights (or areas) per mol of similar size for the two isomers? This information would help to understand potential deficiencies for instrumentation that make combined CFC-114 + CFC114a measurements if reference material differed greatly in composition compared to air samples.

section 3.3 Calibration: pure mixture by DuPont: Could the authors (within confidentiality agreements) provide more details on when (which year) the sample was obtained, if the CFC-114a impurity in CFC-114 production may be constant, which factory it may have been produced (when)?

page 6 line 1: why is 'of known atmospheric abundance' important? Shouldn't it rather say that a compound was used for which independent calibration exists. Was the comparison with NOAA (2.4%) giving a systematic offset for all 3 samples, and which way, which CFC-12 was higher, the calculated or measured? If the 2.4% is considered to be the accuracy for this CFC-114/a calibration scale, it should be stated clearly (the discussion of uncertainty in a later part of the manuscript suggests so).

page 6, line 10: One cannot analyze a 'data set' on a GCMS.

p. 6, line 14: What about the data by Oram (1999), how were these converted? Was Oram (1999) on a preliminary scale? If so, would Lee (1994) mention the difference between scale defined in that thesis and the data published by Oram (1999)? Could the Oram (1999) data be directly converted to the new UEA scale, and if so, what factor, and is it linear. Does UEA plan to give a name to the 'new' scale so to avoid confusion between the past and potential future calibration scales?

page 7, line 14 'at the time'. Why has the model not been re-run with newly-available data? Can the authors assess the error involved with that?

page 7, line 17: incomplete sentence.

page 7, line 24: Can you (perhaps in parenthesis) add the numerical value for the height of the model domain?

page 8, line 3: double mentioning of 'for CFC-114'.

page 8, line 4, 'similar relative range'. Could you be more quantitative?

page 9, line 28: wouldn't it be more appropriate to write 'as emissions of the latter continue to increase'.

page 11, line 26: Provide station name and coordinates.

page 12, line 21: Arent the GWPs given by Harris et al. (vs Carpenter et al)? I couldn't find the value of 8490 in either of the two publications.

references: several obvious errors, check ms carefully: Baasandorj 2013: space missing; Buizert: 55 Sturges; Marsh: lower case words if a journal article, same for other references (e.g. Laube 2014, Sturges (2012); Subscripted numbers in chemical formulae (Oram 1999), Oram (2012)

Figures: The figures would greatly benefit from red-coloring of the axis label numbers and text for CFC-114a

Supplement: Provide a title for the Supplement including the manuscript title, authors etc.

Supplement: Provide numerical results of all flask measurements and the major calculation results (e.g. yearly emissions and uncertainty bands).

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