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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.

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Similar to referee #1 we would like to thank this reviewer for her/his work which has led to a further improvement of this manuscript. Below please find responses to all comments.

Referee comment

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?).

Author response

We recommend Banks et al., 1994 (as cited in the manuscript) for more details on HFC production pathways but consider this level of detail outside the scope of this study. Information on HFC production locations including emissions on an individual country and/or compound basis is not publicly available.

Referee comment

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 âĂŤ 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.

Author response

As mentioned in the manuscript the initial calibration of CFC-114 and CFC-114a was explained in the PhD thesis of Lee (1994). We do not use any further data from that thesis and only cite two non-peer-reviewed works (Lee (1994) as well as Oram (1999)) as they provided crucial input to two peer-reviewed publications, both of which are discussed in detail.

Referee comment

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 misleading to call this a ’pure’ calibration difference.

Author response

As explained in the manuscript, Sturrock et al. compared CFC-114 measurements from two independent sources: 1) from Antarctic firn air and b) from the Cape Grim archive. Isomers were not separated and are based on an AGAGE calibration scale for the former. We have revised the sentence as follows:

“Their firn air-based data (calibration first reported in Prinn et al. (2000)) were compared with University of East Anglia. . .”

Referee comment

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.

Author response

We thank the reviewer for raising this important point. To address this request we have assessed three measurement days which spanned a large range of mixing ratios measured (CFC-114: 1.08 - 15.85 ppt, CFC-114a: 0.08 -1.09 ppt). On m/z 134.96 CFC-114a had a 2.30 ± 0.02 larger area response per ppt measured. This does however appear to be a column-specific response factor. A comparison of other CFC isomers (CFC-112, CFC-112a, CFC-113 and CFC-113a) has already revealed that mixing ratios of one isomer could be used to predict those of the other within 23 % on the Agilent GS GasPro column (Kloss et al., 2014). In contrast when determining the molar responses of one of these isomer pairs on the KCl-passivated AlPLOT column (i.e. CFC-113 and CFC-113a as the CFC-112 isomers are not separated) these were very different from expectation i.e. 2.89 instead of 1.68 as expected from the mass

spectra. Nevertheless the mixing ratios of CFC-113 and CFC-113a derived from measurements using the two different columns agree very well. Coming back to the original question we have therefore not included these results in the manuscript but will offer our support to anyone wishing to investigate historical results (e.g. through comparison experiments).

Referee comment

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)?

Author response

The sample was obtained in 2014 but the additional details could unfortunately not be obtained.

Referee comment

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).

Author response

The CFC-12 mixing ratios determined via the UEA system were between 1.6 and 2.4 % higher than the mixing ratios based on the NOAA scale. We have altered the statements to “A CFC for which an independent an internationally recognised calibration exists. . .” and “The three separate calibration analyses were accurate to within 2.4% of NOAA values (using CFC-12 mixing ratios, 2006 NOAA scale) and we therefore consider the accuracy of the calibration to be 2.4% at the most. As for the calibration precision the 1σ standard deviation of these calibrations was 1.2 % (CFC-114) and 1.5% (CFC-114a) respectively."

Referee comment

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

Author response

We have altered the statement to: "Both of these data sets originate from measurements on a previous version of the GC-MS system. . ."

Referee comment

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?

Author response

As pointed out above neither of the two works are peer-reviewed literature. To clarify, both Oram (1999) and Lee (1994) provided results based on the same calibration scale.We have changed the statement to "The conversion factor from the old calibration scale (Lee, 1994 and Oram, 1999) as published. . ." The transfer is linear as can be concluded from the following statement: "To ensure comparability of the data sets, 14 Cape Grim samples collected between 1978 and 2004 have been analysed on both systems and these data agree within uncertainties for both isomers and show no indication for any systematic offset. " The request to name the new scale has already been addressed. Please the respective response to reviewer #1.

Referee comment

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?

Author response

We have, in the revised version, taken into account the newly published absorption cross section data for CFC-114a by Davis et al. (2016). By re-running the model with the Davis et al. (2016) absorption cross section data, the emissions of CFC-114a have slightly reduced in comparison to the old emissions derived using absorption cross section data by Simon et al. (1988). Also, we have revised the lifetime of CFC-114a from 100 years to 102 years. The latter lifetime is in agreement with the WMO latest recommendation for the lifetime of CFC-12. However, most of the loss of CFC-114a is outside the model domain and so the F value (as explained in the manuscript) has been changed to 0.837, so that the model will give the right lifetime. The range of lifetimes for CFC-114a has also been revised accordingly i.e. from (80 -130 years) to (82 - 133 years). Using the new lifetime and photolysis data has overall caused very small changes to the emission estimates of CFC-114a with equally small knock-on changes to the derived emissions of the sum of the isomers (Figure 4) and the emission ratios displayed in Figure 2. None of these changes alters the overall conclusions of the paper.

Referee comment

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

Author response

We have included the numerical values (82 - 133 years) as requested.

Referee comment

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.

Author response

We have corrected the statement two-fold: 1) The GWP was reported by Hodnebrog et al., 2013, which has been added to the reference and 2) The number in the text was wrong and has been changed to 8,590 (the calculation was correct).

Referee comment

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

Author response

The numerical value is 24 km which is already quantified in the manuscript: “The model comprises of grid boxes which have been equally divided into 24 equal-area, zonally-averaged bands and has 12 vertical layers of 2 km depth.”

Minor suggestions/corrections:

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

page 7, line 17: incomplete sentence.

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

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.

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).

Author response

All changes were made as requested.

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