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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.

Johannes C. Laube et al.

j.laube@uea.ac.uk

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We would like to acknowledge the work of the anonymous reviewer and her/his detailed comments which have helped to further improve this manuscript. Below please find responses to all comments.

Referee comment

P5 Calibration – what calibration scale are CFC-114 and CFC-114a reported on?

Author response

As explained in section 3.3 this is a UEA-made calibration scale using our established

volumetric calibration system which minimises differences to gravimetric methods. We have named these and modified the following statements to make this clearer: "Older data had to be transferred to the new calibration scales ("UEA-2014") using repeatedly measured ratios between internal standards. The conversion factor from the old UEA calibration scale (Lee, 1994)..."

Referee comment

P5 L18 Is it reasonable that the average sample precision is 1.1% for both isomers considering one isomer is 14-22x more abundant than the other, and the mole fraction of the samples has increased from 7.9 to 14.8 (CFC-114) and 0.35 to 1.03 (CFC- 114a) over time.

Author response

The detection limits of our analytical system are in the sub-ppq range (e.g. Kloss et al., 2014), so the signal-to-noise ratio is not the limiting factor for precisions of either isomer – not even for the deepest firn samples which have as small mixing ratios as 0.06 ppt for CFC-114a.

Referee comment

P5 L26 What is the quoted uncertainty associated with the DuPont sample?

Author response

The sample was provided at >99.8 % purity (weight) as determined by GC-FID and contained small amounts of other trace gases, most notably 0.112 % of CFC-115 and 0.028 % of CFC-13. The latter were successfully removed to below detection limits through transfer into a vacuum-tight canister followed by repeated freezing and evacuating cycles (see statement: "The same dilutions were also analysed in full scan mode to ensure their purity"). This information was added to section 3.3.

In addition our calibration depends heavily on the accuracy of the ratio of CFC-114

and CFC-114a in that sample. DuPont provided no further information with regard to this matter. It is however well known that the molar response factors of isomeric compounds are very similar in Flame Ionisation detectors (e.g. Tong and Karasek, 1984). Nevertheless we have added a respective statement to section 3.3:

“It should also be noted that the accuracy of our calibration is limited by the accuracy of the ratio of CFC-114 and CFC-114a in the sample provided by DuPont, which is unknown. It is however well known that the molar response factors of isomeric compounds are very similar in Flame Ionisation detectors (e.g. Tong and Karasek, 1984), so this is unlikely to be a major limitation of this study.”

Referee comment

P5 L31 Use of epoxy resins cover a wide range of potential chemicals and by-products - are the authors sure that no contamination has been introduced to the calibration drums?

Author response

The internal drum surface area exposed to the resin is minimal. In addition the dilution drums were flushed with > 20,000 litres of Nitrogen and no major additional organic compounds were detected in the subsequent blanks. We have added this information to the manuscript and also note that epoxy resin has been successfully used to seal canisters of the whole-air-samplers operated on board the CARIBIC aircraft for more than a decade, including the successful measurement of a large variety of halocarbons and hydrocarbons (Brenninkmeier et al., 2007).

Referee comment

P7 L8 On what evidence is the assumption about latitudinal distribution of CFC-114/114a made?

Author response

The latitudinal distribution is based on the work by McCulloch et al. (1994) which has been added to the manuscript. This emission distribution has been used previously to study the temporal behaviour and global distribution of other long-lived halocarbons (e.g. Reeves et al., 2005, Kloss et al., 2010, Laube at al., 2010, Oram et al., 2012, Newland et al., 2013, Laube et al., 2014). Specifically Reeves et al. (2005) showed that for CFC-11 and CFC-12 the model, with this emission distribution, reproduced southern hemispheric observations to within about 5%.

Referee comment

P7 L17 There appears to be some missing text? "based on work by and".

Author response

Both the sentence “The recommended values mentioned above are based on work by and.” and the text above it are intended to convey a similar message. Hence, sentence and text have been revised as follows:

"The rate coefficients of 1.43 x 10-10 cm3 molecule-1 s-1 and 1.62 x 10-10 cm3 molecule-1 s-1 are applied to the reaction of O(1D) with CFC-114 and CFC-114a, based on work by Baasandorj et al. (2013) and Baasandorj et al. (2011), respectively.“

Referee comment

P7 L29-32. The quoted uncertainties appear quite small especially 5% for modelling uncertainties. Can the author describe more fully how uncertainties have been derived?

Author response

The modelling uncertainty was estimated to be 5% based on previous work with the model. Generally, the model is able to recreate measurements of long-lived gases at Cape Grim with mainly northern hemisphere emissions and well-established emission histories (e.g., CFC-11, CFC-12) to within 5%.

Referee comment

Figure 2. How can you be sure that the rapid change in ratio of CFC-114a/CFC-114 is not driven by emissions from Asia/Taiwan as detailed in Figure 6?

Author response

The caption of Figure 2 does not claim any reasons for this rapid change. We do provide strong indications in the main text that the ratio change from the 1990s onwards is connected to HFC-134a production. The reviewer is also correct that Figure 6 provides indications for continuing emissions of CFC-114a from East Asia. We do however have no evidence that East Asian HFC production was driving those ratio changes, from the 1990s onwards. This is in fact unlikely as there is and was substantial production of HFC-134a outside of East Asia.

Referee comment

P1 L22 The global ban came into force in 2010 but non-A5 countries in 1996.

Author response

Our statement is correct and has been kept concise for the abstract. The 1996 date is included later in the manuscript.

Referee comment

P1 L37 36 year period

Author response

The period is inclusive of both 1978 and 2014.

Minor suggestions/corrections:

P1 L36 increased from 4.2% to 6.5%

P3 L30 Chan et al., 2006 not 2007

P4 L6 missing a closing bracket) to close (clean marine ...)

P5 L5 Can you provide the details of the column supplier, diameters, length and film thickness.

P4 L16 Fraser at al., 1986 is not listed in the references?

P14 L30 need full author list not just et al.:

Figure 1. The way the two y-axes are plotted makes the CFC-114 and CFC-114a trends appear to converge between 1980-1990. Can the scales be adjusted to allow the trends and uncertainties to be viewed more easily?

Author response

All changes were made as requested.

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