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Comment

Interactive comment on “Rapid growth of HFC-227ea (1,1,1,2,3,3,3-Heptafluoropropane) in the atmosphere” by J. C. Laube et al.

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General comments

Referee comment

The standardization of the measurements plays a major role in this work, especially since one of its principal results is that actual emissions appear to be very significantly less than has been estimated from “bottom-up” methods (e.g. by EDGAR). Yet there is no discussion of this in the main paper – not even a calibration uncertainty estimate appears there. It appears only in the Supplemental Information, but because of the importance of the absolute values to the conclusions, I believe that a brief summary of calibration and calibration uncertainty (15%) belongs in the main paper. The cali-

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bration section that is in the Supplemental Information section is importantly in need of revision because of a fundamental inconsistency in the units in which the HFC-227ea measurements are reported. Throughout the main paper, the units that are given are “pptv” (parts-per-trillion by volume), but in the Supplemental Information (p. 2, lines 6-10) it is explained that the standards were prepared volumetrically and reported as dry air mole fractions assuming that the gases from which the standards were made follow the ideal gas approximation. They do not. The PVT properties of HFC-227ea have been measured and are reported in the literature (Y. Y. Duan et al. (2001), Thermodynamic Properties of 1,1,1,2,3,3,3-Heptafluoropropane, Int. J. Thermophysics, 22, No. 5, 1463-1474). The second virial coefficient of HFC-227ea at 25 °C is reported to be -661 cm³, or about 3% of the volume of the gas at 1 atm and room temperature. In fact, the assumption that the ideal gas approximation applies is incorrect, and the reported values are not dry air mole fractions as is claimed. Rather, the reported values are indeed volume ratios, but volume ratios given without defining the pressures or temperatures at which the volumes were measured. To make the reporting credible, the authors should make their best effort to report the values as actual dry air mole fractions, explain how the calculation was done in the Supplemental Information, and use the correct mole fraction unit of “ppt” (without the “v”) or “nmol/mol”. The “pptv” designation appears in many places in the main paper, in figures, and in the Supplemental Information. All of these should be changed, and it should say in the main paper that the data are reported as dry air mole fractions. In order to do the comparison with the NOAA CF₂Cl₂ standard that is described in the Supplemental Information properly it will be necessary to correct for the non-ideality of CF₂Cl₂ in the volumetric mixtures also. Otherwise it is an “apples to oranges” comparison.

Author response

A brief summary of the calibration was added to the manuscript: “To evaluate this system CF₂Cl₂ was added as an internal reference and diluted similarly. The resulting mixing ratios (which are dry air mole fractions) agreed with the internationally recog-

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nized calibration scale of NOAA (2001 scale) within 1.3 %. Summing up all uncertainties that could affect the calibration values gives about 15 %. However, taking into account the good agreement with the NOAA scale for CF₂Cl₂ as well as the small variability between calibrations for HFC-227ea (< 4 %) we estimate our scale uncertainty to be not larger than 5 %.” Although the overall coverable pressure range was given in the manuscript (50 to 300 mbar) we agree with the referee, that the actual parameters and calculations used to derive the mixing ratios of HFC-227ea should have been explained in more detail. Thus the revised version of the supplement contains the following additional information: “For the pressures, temperatures (between 80 and 130 mbar at 80 °C) and compounds used the systematic errors introduced by assuming ideal gas conditions are between 0.09 and 0.20 % (calculated by using virial coefficients from Duan et al., 2001 for HFC-227ea and from Schramm et al., 1992 for CF₂Cl₂). We applied the respective corrections in order to report dry air mole fractions but also note that these errors are far smaller than the accuracy and precision of our determinations here. Eq. S1 summarises the calculation of mixing ratios for the first dilution step. In addition, we replaced “pptv” by “ppt” throughout the manuscript. Finally we would like to point out that it is - with regard to the rather small corrections - in our opinion inappropriate to speak of an “apples and oranges” comparison.

Referee comment

In the analysis section (p. 7679, line 6-24) it should say somewhere whether HFC-227ea was separated from all co-eluting more-abundant substances sufficiently well to eliminate concerns over quenching of the mass spectrometer source efficiency, which could have the effect of reducing the sample/standard ratio if any such substances were not in the standard but were in natural air.

Author response

It is clearly stated in the respective section, that “No chromatographic interferences were found for these ions at the given retention time window.”.

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Referee comment

All of the trends derived from measurements of air entrapped in firn are dependent on the assumption that HFC-227ea is conservative in the firn over the time periods represented by the measured trends. This applies to chemical destruction mechanisms and to physical processes such as adsorption or dissolution into the firn ice. This is a problem inherent to all such firn studies, and the assumptions that are made need to be stated explicitly, probably in the first paragraph of Section 3.1.

Author response

The requested statement was added: “Please note, that all of the trends derived from measurements of air entrapped in firn are dependent on the assumption that the respective compound is chemically (no destruction) and physically (no adsorption or dissolution) unaffected in the firn over the time periods represented by the measured trends.”

Technical Comments

Referee comments

Title: I agree with another of the reviewers that the subjective word “Rapid” could be left off of the title.

P. 7677, line 4: Delete “rapid”.

Author response

Both phrases were changed to “accelerating growth”.

Referee comments

P. 7677, lines 19-20: Do not capitalize chlorofluorocarbons or hydrofluorocarbons.

P. 7677, line 23: Delete “i.e.”.

P. 7678, line 7: All GWPs are relative to CO₂, so delete “as relative to CO₂”.

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P 7678, line 9 and elsewhere: I agree with another reviewer that the EDGAR citation should be simplified.

P 7679, line 8: Do not capitalize gas chromatography or mass spectrometric (also p. 7680, line 14).

Author response

Changes were applied as requested.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 7675, 2010.

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