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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.

Anonymous Referee #2

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General Comments

Because this paper reports the first measurements of a new industrially produced compound in the atmosphere, it should be published. It includes a diverse approach to assessing the growth rate, and hence the emission rate, of HFC-227ea into the atmosphere, including measurements in firn air, in the contemporary atmosphere, and in the lower stratosphere. It also includes a clever assessment of the stratospheric lifetime of HFC-227ea. I believe that APC is an appropriate venue for the publication of this work – which I fully endorse – although I do have a number of comments that I believe ought to be taken into account before publication. Among these, the first comments concerning calibration and units are critical and should not be compromised.

Specific Comments

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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 calibration 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 cm^3 , 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.

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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.

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.

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.

Technical 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”.

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”.

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.

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7680, line 14).

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

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