

Interactive comment on “Long-term tropospheric trend of octafluorocyclobutane (c-C₄F₈ or PFC – 318)” by D. E. Oram et al.

D. E. Oram et al.

d.e.oram@uea.ac.uk

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We thank the reviewer for their constructive comments and respond to specific questions below.

P 19090, Line 11, I do not feel that the origins of this compound are unclear. It is widely reported

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that this anthropogenically released compound is used as a chamber cleaning gas in PECVD chambers, in the semi-conductor industry for di-electric etching and with a host of other minor usages. What is unclear from this paper is why the bottom up emission estimates are so different to the estimates determined from atmospheric observations.

Author response:

We have replaced the sentence “The origins of c-C4F8 are unclear” with “Although a number of potential sources of c-C4F8 have been reported, including the electronics and semi-conductor industries, there remains a large discrepancy in the atmospheric budget”.

P 19091, Line 26, the citation for Ravishankara et al., 1993 is missing from the references:

AR: Reference has been added.

P19094, Line 10, Can the author provide some statistics or at least describe how the magnesium perchlorate trap was shown to have no effect on the concentration data?

AR: The magnesium perchlorate (MPC) dryer was tested by trapping and analysing dry air samples both with and without the MPC dryer. There were no discernable differences for c-C4F8 and many other halocarbon gases as has been widely reported elsewhere.

P19094, Line 29, Although the agreement was within 3% with no significant bias for comparison data between 1999 and 2005, it is possible that agreement between methods (and bias) might be more pronounced for earlier flask analysis. For flasks collected between 1978 and 1998, the

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atmospheric abundance of c-C₄F₈ was appreciably lower, and analysis was carried out using a lower sample volume (post 2006 sample volume is 50% higher).

AR: We cannot rule out a discrepancy between the two analytical systems in samples collected before 1998. Unfortunately we have not been able to reanalyse these earlier samples yet, although we would expect to do so sometime in the future. For the current paper we have been able to demonstrate an excellent agreement between the two analytical systems over a period of at least 10 years. Furthermore, any earlier discrepancy would not affect current atmospheric concentrations, trends or emission rates. It does not therefore alter the main message of the paper.

P19094, Line 5-9, Does the UEA scale have a name and a reference year, this would aid future

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comparisons of data from other groups who might measure c-C4F8?

AR: We have defined the calibration scale as UEA-2010.

P19094, Line 28, Can the author describe how a figure of 7% uncertainty is determined for the UEA calibration scale?

**AR: As indicated in the paper, the methods used for deriving the uncertainty in the calibration scale are described in detail in Laube et al. (2010a). We thought it was probably unnecessary to repeat all the details again, so chose to highlight only the differences between the c-C4F8 and HFC-227ea calibrations. We have changed the text to read “The total uncertainty of the UEA calibration scale for c-C4F8 is estimated to be no greater than 7%,
... .”**

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P19095, Line 2-5, What were the errors that caused the old UEA scale for c-C4F8 to produce atmospheric measurement mixing ratios 19.6% higher than the newer scale, this appears to be a very large difference.

AR: The previous calibration was performed many years ago (mid-1990s) with a substantially different calibration system. It is not possible for us to evaluate the cause of the ~20% discrepancy. The current calibration system is certainly more precise than the earlier system, due to the improvements in dispersing pure vapours into the mixing chambers at low pressures and in the use of internal reference compounds such as CFC-12.

P19096, Line 14-19, You calculate growth rate for 2003-2008 by using a linear fit and then compare this to the growth rate between 1990-2002. What type of fit is used for the 1990-2002 period? Why

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choose to compare this period with 2003-2008, when you also state that during the early 1990s growth slowed then increased again since 1996?

AR: We thank the reviewer for spotting this mistake. The text has been modified to read: “The growth rate of c-C4F8 has fluctuated over this 30 year period, slowing considerably during the late 1980s, but increasing again since ~2002. A linear fit through the 2003-2008 data ($R^2 = 0.91$) yields a growth rate of 0.030 ± 0.002 ppt yr⁻¹, or 2.7 % yr⁻¹ based on the mean 2008 mixing ratio of 1.12 ppt. This is significantly higher than the 0.016 ± 0.001 ppt yr⁻¹ seen between 1990 and 2002 (linear fit, $R^2 = 0.81$).”

P19097, Line 7, Synoptic variation, short timescale dynamics, stratospheric-tropospheric exchange and interhemispheric transport and interannual variability will all effect data acquired at the Cape

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Grim site. How are these effects dealt with by the 2D global chemistry transport model employed to analyse the data, especially since no physical measurements are made in the northern hemisphere at the same time as the Cape Grim measurements?

AR: We use a 2-D model with zonally-averaged latitude bands. The model incorporates an idealised transport scheme which changes seasonally but is repeated from year to year. It is based on climatological met data so does not allow for year-to-year variability in interhemispheric exchange, etc. One of the main reasons for using Cape Grim as a long-term monitoring station is that the air it receives under baseline conditions is very clean, well mixed and representative of mid-latitudinal southern hemispheric air. All Cape Grim samples reported

here were collected during baseline conditions. The model's transport scheme has been thoroughly tested using long-lived tracers such as the CFCs and has proven to be very successful in reproducing the southern hemispheric concentrations of long-lived tracers that are primarily emitted in the northern hemisphere (Hough, 1989; Reeves et al. 2005).

P19097, Line 11-13, what evidence is there that the industrial usage of c-C4F8 result in 95% of emissions in the Northern Hemisphere? Is it not possible that the function of industrial activity has changed since Reeves et al., 2005?

AR: Of course it is not possible to know with total certainty that 95% emissions of c-C4F8 occur in the northern hemisphere or whether this distribution may have changed with time, particularly as we do not know the exact sources

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of the “missing” c-C4F8. According to the EDGAR database, less than 1% of reported 2005 emissions occurred in the southern hemisphere, although no data is available from South America or Africa. Because of the nature of the model (2-D, zonally-averaged), small changes in the release distribution of a long-lived tracer such as c-C4F8, especially northern hemisphere changes, have a very minor effect on the observed concentrations in the latitudinal band of Cape Grim. What is clear is that the uncertainty in the emission distribution cannot account for the very large discrepancy between the top-down and bottom-up emissions presented here. Because of these uncertainties we decided to stick with the distribution described in Reeves et al. (2005).

P19097, Line 21, Can you provide a reference for the 1yr inter-hemispheric mixing, many studies

have used longer times than this, how sensitive is your analysis to changes inter-hemispheric mixing?

AR: In order to display the CARIBIC data in the same time context as the Cape Grim data in Figure 1 it was necessary to make an allowance for interhemispheric exchange time, as the CARIBIC data from 1998 and 1999 are from the NH, whilst Cape Grim is at 41°S. We agree that normally one would use a slightly higher interhemispheric exchange time than 1 year, but in this case we chose a value of 1 year as most of the CARIBIC data was collected at low latitudes and in the Tropics. However, the comparison is intended for illustrative purposes only, as we do not use the early CARIBIC data for any growth rate or modelling calculations. As discussed above (P19097, Line 7), the 2-D model uses a climatological mixing/transport scheme and is not

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able to deal with “real world” year-to-year changes in interhemispheric mixing times. Furthermore, as stated in the previous response (P19097, Line 11-13), small changes in the emission distribution for long-lived tracers make only very small changes to the modelled concentrations at Cape Grim.

P19100, Line 23-25, The CARIBIC flight data for the Southern Hemisphere mean produce values growth values that are higher and outside of the uncertainty estimates that are indicated by the Cape Grim record. The reported Cape Grim mid-2008 mixing ratio was reported as 1.1ppt with a linear growth rate of 0.03 ppt/yr, this would produce a mid-2009 value of 1.13ppt and mid-2010 value of 1.16ppt, the CARIBIC flight produced values in 2009 of 1.18 ± 0.02 ppt and 2010 values of 1.20 ± 0.01 ppt. This would suggest a linear growth

rate of ± 0.04 - 0.05 ppt/yr?

AR: We only report a growth rate of 0.03 ppt/yr for the period 2003 to 2008. We do not know what the growth rate at Cape Grim would have been after this, making direct comparison with CARIBIC data in 2009 and 2010 inappropriate. It may be that the growth rate has simply increased again. The reviewer is also trying to compare surface data from Tasmania with aircraft data collected at 10-12 km and at lower latitudes over Southern Africa, so small differences of the order of 0.02 ppt would be entirely reasonable.

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