



# Long-term tropospheric trend of octafluorocyclobutane (c-C<sub>4</sub>F<sub>8</sub> or PFC-318)

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Received: 18 May 2011 – Published in Atmos. Chem. Phys. Discuss.: 4 July 2011

Revised: 2 November 2011 – Accepted: 21 November 2011 – Published: 5 January 2012

**Abstract.** Air samples collected at Cape Grim, Tasmania between 1978 and 2008 and during a series of more recent aircraft sampling programmes have been analysed to determine the atmospheric abundance and trend of octafluorocyclobutane (c-C<sub>4</sub>F<sub>8</sub> or PFC-318). c-C<sub>4</sub>F<sub>8</sub> has an atmospheric lifetime in excess of 3000 yr and a global warming potential (GWP) of 10 300 (100 yr time horizon), making it one of the most potent greenhouse gases detected in the atmosphere to date. The abundance of c-C<sub>4</sub>F<sub>8</sub> in the Southern Hemisphere has risen from 0.35 ppt in 1978 to 1.2 ppt in 2010, and is currently increasing at a rate of around 0.03 ppt yr<sup>-1</sup>. It is the third most abundant perfluorocarbon (PFC) in the present day atmosphere, behind CF<sub>4</sub> (~75 ppt) and C<sub>2</sub>F<sub>6</sub> (~4 ppt). Although a number of potential sources of c-C<sub>4</sub>F<sub>8</sub> have been reported, including the electronics and semi-conductor industries, there remains a large discrepancy in the atmospheric budget. Using a 2-D global model to derive top-down global emissions based on the Cape Grim measurements yields a recent (2007) emission rate of around 1.1 Gg yr<sup>-1</sup> and a cumulative emission up to and including 2007 of 38.1 Gg. Emissions reported on the EDGAR emissions database for the period 1986–2005 represent less than 1 % of the top-down emissions for the same period, which suggests there is a large unaccounted for source of this compound. It is also apparent that the magnitude of this source has varied considerably over the past 30 yr, declining sharply in the late 1980s before increasing again in the mid-1990s.

## 1 Introduction

Owing to a combination of long atmospheric lifetimes and strong absorption bands in the infrared, fully fluorinated hydrocarbons (perfluorocarbons or PFCs) are among the most potent greenhouse gases known, with global warming potentials three or four orders of magnitude greater than that of CO<sub>2</sub> (Forster et al., 2007). Being harmless to stratospheric ozone, PFCs were not included in the Montreal Protocol and no formal international restrictions have been placed on their production and/or consumption. More recently however the PFCs have been included in the suite of gases covered by the Kyoto Protocol.

The most abundant PFC in the atmosphere is CF<sub>4</sub>. The first atmospheric measurements were reported in the late 1970s (Rasmussen et al., 1979) and it has a current tropospheric abundance in the region of 75 ppt (Khalil et al., 2003; Worton et al., 2007; Mühle et al., 2010). Other identified PFCs include C<sub>2</sub>F<sub>6</sub>, first reported by Penkett et al. (1981), C<sub>3</sub>F<sub>8</sub> (Culbertson et al., 2000) and c-C<sub>4</sub>F<sub>8</sub> (Oram et al., 1999; Sturges et al., 2000). The present-day abundances of these compounds are much lower than CF<sub>4</sub>, being typically in the range of a few ppt or less (Khalil et al., 2003; Culbertson et al., 2004; Worton et al., 2007; Mühle et al., 2010; Saito et al., 2010). However, atmospheric levels of all three minor PFCs have been reported as increasing in recent years, as is that of CF<sub>4</sub>.

Historically the primary anthropogenic source of PFCs to the atmosphere has been the aluminium industry, which is known to release CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> during the electrolytic

reduction of aluminium oxide to aluminium. More recently PFCs have found increasing usage in the electronics industry, where they are used in the manufacture of semiconductors (plasma etching, chamber cleaning, etc.). Recent studies of air trapped in ice cores and polar firn have revealed that CF<sub>4</sub> has a natural background of around 35 ppt, approximately half of its present day abundance (Harnisch et al., 1996; Worton et al., 2008; Mühle et al., 2010). Harnisch and Eisenhauer (1998) found evidence for the slow release of CF<sub>4</sub> from rocks containing natural fluorites and have suggested that degassing from the Earth's crust could sustain this natural background, although the annual natural source is miniscule relative to present day anthropogenic sources.

Long term trends of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> have been reported in the recent literature (Mühle et al., 2010) but there remains little information on another PFC, octafluorocyclobutane (c-C<sub>4</sub>F<sub>8</sub>, or PFC-318). In common with other perfluorinated compounds, c-C<sub>4</sub>F<sub>8</sub> is resistant to the common atmospheric degradation mechanisms, resulting in an estimated lifetime of 3200 yr (Ravishankara et al., 1993). Furthermore, it is a strong greenhouse gas with GWPs of 7310, 10 300 and 14 700 for 20-yr, 100-yr and 500-yr time horizons respectively (Forster et al., 2007), making it one of the most potent greenhouse gases to be identified in the atmosphere to date. Saito et al. (2010) recently reported measurements of c-C<sub>4</sub>F<sub>8</sub> from two Japanese sites in the Northern Hemisphere over the period 2006–2009. Mean baseline mixing ratios of 1.33 pptv and 1.22 pptv were observed at Hateruma Island (24.1° N, 123.8° E) and Cape Ochiishi (43.1° N, 145.3° E) respectively, with corresponding growth rates of 0.02 and 0.01 pptv yr<sup>-1</sup>.

Here we report observations of c-C<sub>4</sub>F<sub>8</sub> between 1978 and 2008 from a long term measurement programme at Cape Grim, Tasmania. These data are complemented by more recent measurements in the upper troposphere and lower stratosphere from samples collected by the CARIBIC and Geophysica aircraft. The long-term southern hemispheric trend is used to derive a top-down global emission scenario using a 2-D atmospheric model. The model-derived emissions are compared with those reported to the EDGAR database.

## 2 Experimental

A total of 110 air samples from Cape Grim, Tasmania (41° S, 145° E) have been analysed for their c-C<sub>4</sub>F<sub>8</sub> content. The majority of samples since 1994 have been collected directly into 3-l electropolished (Rasmussen) or Silcosteel-treated stainless steel canisters (Restek Corp.) at a pressure of ~3 bar using a diaphragm pump (KNF). Prior to 1994, the samples analysed were sub samples of the parent Cape Grim air archive. Details of the archive and the sampling techniques have been reported elsewhere (Langenfelds et al., 1996; Oram et al., 1995; Fraser et al., 1999). Trace gas data (CFC-11, -12, -113, CH<sub>3</sub>CCl<sub>3</sub>, and CH<sub>4</sub>) obtained from the

archive show the same concentrations and long term trends as in-situ measurements at Cape Grim for the same species (Cunnold et al., 1994; Prinn et al., 1995), indicating that the archive contains representative samples of background air and, importantly, that these species can be stored without significant changes in their concentration. The archive has been used to reconstruct the past atmospheric history of halons (Fraser et al., 1999); HCFCs-141b (CH<sub>3</sub>CFCl<sub>2</sub>) and -142b (CH<sub>3</sub>CF<sub>2</sub>Cl) (Oram et al., 1995); HCFC-22 (CHClF<sub>2</sub>) (Miller et al., 1997); HFC-134a (CF<sub>3</sub>CH<sub>2</sub>F) (Oram et al., 1996); CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> (Mühle et al., 2010) and SF<sub>6</sub> (Maiss et al., 1996). Being highly inert and with similar properties to other long-lived halocarbons, we are confident of the stability of c-C<sub>4</sub>F<sub>8</sub> in the archive samples.

Prior to analysis, the Cape Grim samples (~200 ml) were pre-concentrated using a stainless steel manifold. After drying, by passing through magnesium perchlorate, condensables were trapped in an evacuated, 100 × 3 mm OD stainless steel sample loop filled with 100 μm glass beads, held in liquid argon (−186 °C). The bulk of the air passed into an evacuated stainless steel flask (~800 ml), where the pressure change, and hence sample volume, was measured with a capacitance manometer (Edwards Barocel). The magnesium perchlorate trap was shown to have no effect on the measured c-C<sub>4</sub>F<sub>8</sub> concentrations.

Up until 2006 all samples were analysed using a double-focussing, tri-sector mass spectrometer (V.G. Autospec) coupled to the outlet of a Hewlett Packard 5890A gas chromatograph. The mass spectrometer was operated in electron ionisation, selected ion mode at a resolution of ~2000. c-C<sub>4</sub>F<sub>8</sub> was monitored at *m/z* 130.992, which corresponds to the C<sub>3</sub>F<sub>5</sub><sup>+</sup> ion, the most abundant ion in the mass spectrum. Various halocarbons, including c-C<sub>4</sub>F<sub>8</sub> (retention time ~10.4 min), were separated on a KCl-passivated alumina PLOT column (50 m × 0.53 mm, Chrompack), with helium carrier gas (2 ml min<sup>-1</sup>) and a temperature program of −10 °C (2 min) rising to 180 °C, at a rate of 15 °C min<sup>-1</sup>. Full details of the method can be found in Fraser et al. (1999). Since 2006 samples have been analysed using a similar method but with an updated GC-MS (Waters Autospec Premier) and a slightly modified pre-concentration procedure. The post 2006 procedures are described in detail by Laube et al. (2010a), but the main changes are in the method of pre-concentration, which now incorporates a Hayesep D-packed stainless steel sample loop at −78 °C, and the chromatographic column (Agilent 30 m × 0.32 mm GS-GasPro). A selection of pre-2006 samples (~300 ml) have been reanalysed with this system to confirm the absence of systematic differences. Comparisons of 6 samples covering the period 1999–2005 showed agreement to within 3 %, with no significant bias.

The mean precision of 2–3 replicate analyses, bracketed by working standard samples to correct for instrumental drift, was 0.8 %, based on the pre and post 2006 methods. Blank tests were performed by analysing 200–300 ml of purified

helium (the carrier gas).  $c\text{-C}_4\text{F}_8$  was below the detection limit ( $\text{DL} < 0.01$  ppt) in these blank tests.

The working standard used to calibrate the pre-2006  $c\text{-C}_4\text{F}_8$  data was a northern hemispheric air sample collected at Niwot Ridge, Colorado, USA, contained in an Acufite-treated, aluminium cylinder (ALM-39753) at an initial pressure of  $1.3 \times 10^4$  kPa (supplied by J. Elkins, NOAA-ESRL, Boulder, Colorado, USA). A different working standard, also from NOAA, was used for the post 2006 analyses (AAL-071170). The concentration of  $c\text{-C}_4\text{F}_8$  in this second working standard ( $1.55 \pm 0.04$  ppt) was determined by three repeated comparisons to primary standards prepared using a two stage static dilution technique described recently in Laube et al. (2010a). The stated purity of the  $c\text{-C}_4\text{F}_8$  used for the dilutions was 99 % (Fluorochem Ltd. UK) and the absence of impurities was confirmed by performing a mass scan over the range 47–200 amu. Three separate dilutions in the region of 6–14 ppt were prepared using  $\text{CF}_2\text{Cl}_2$  (CFC-12, 16–30 ppt) as an internal reference. The  $\text{CF}_2\text{Cl}_2$  mixing ratio assigned to the working standard from these dilutions was within 4.6 % of the value assigned by NOAA (2001 scale). The concentration of  $c\text{-C}_4\text{F}_8$  in the original working standard (ALM-39753;  $0.91 \pm 0.03$  ppt) was determined by repeat comparisons to AAL-071170. The UEA calibration is based on volumetric dilutions and therefore generates standards on a pptv scale. To convert to a dry air mole fraction scale (ppt) the UEA scale has been corrected for non ideal gas behaviour. As described in Laube et al. (2010a) the correction under the reduced pressures of the initial dilution step is actually very small, in the case of  $c\text{-C}_4\text{F}_8$  being less than 0.2 %, based on the virial coefficients reported by (Douslin et al., 1959). The linearity of the pre-concentration and analytical system was tested by pre-concentrating different volumes of the working standard (between 50 and 300 ml) and found to be linear within 1.2 %. The total uncertainty of the UEA calibration scale for  $c\text{-C}_4\text{F}_8$  is estimated to be no greater than 7 %, which is slightly higher than that reported for HFC-227ea (<5 %, Laube et al., 2010a) due to the higher uncertainty of the CFC-12 internal standard (4.6 % for  $c\text{-C}_4\text{F}_8$  dilutions, 1.3 % for HFC-227ea dilutions).

The new calibration scale (UEA-2010) replaces an earlier scale which was used to calibrate previously reported measurements of  $c\text{-C}_4\text{F}_8$  from UEA (Oram, 1999; Sturges et al., 2000; Montzka and Fraser, 2003). These earlier numbers must be reduced by 19.6 % to place them on the current scale.

### Aircraft measurements

Samples from two aircraft programmes have also been analysed for  $c\text{-C}_4\text{F}_8$ . Two recent flights of the CARIBIC aircraft (Lufthansa Airbus 340; <http://www.caribic-atmospheric.com>) between Germany and South Africa were analysed using the GasPro column / Autospec Premier combination. A total of 34 samples were analysed from flights on 27–29 October 2009 (21 samples, Flights 290 and 291) and 14–15

November 2010 (13 samples, Flight 317). One sample was found to be contaminated and rejected. CARIBIC whole air samples are collected in 2.7 l glass vessels at pressures of around 4 bar. Full details of the CARIBIC instrument package and sampling methods can be found in Brenninkmeijer et al. (2007).

Samples collected during two earlier flights of the CARIBIC aircraft have also been analysed for  $c\text{-C}_4\text{F}_8$ . 20 samples from flights on June 5 (9 samples, Flight 5) and August 7 (11 samples, Flight 7) 1998 were analysed using the original instrument and alumina PLOT column. These Northern Hemisphere flights between Germany and Sri Lanka occurred during phase 1 of the CARIBIC project (LTU airlines, Boeing 767), which had a smaller instrument package and a different whole air sampler (see Brenninkmeijer et al., 1999 for details). At this time air samples were collected at high pressure ( $\sim 17$  bar) into 21-l stainless steel cylinders, with aliquots being transferred into smaller (2.5 l) electropolished SS canisters (3–4 bar) for subsequent halocarbon analysis. The lack of variability in the data and excellent agreement with the Cape Grim measurements (see below) confirms the reliability of the sampling and subsampling techniques.

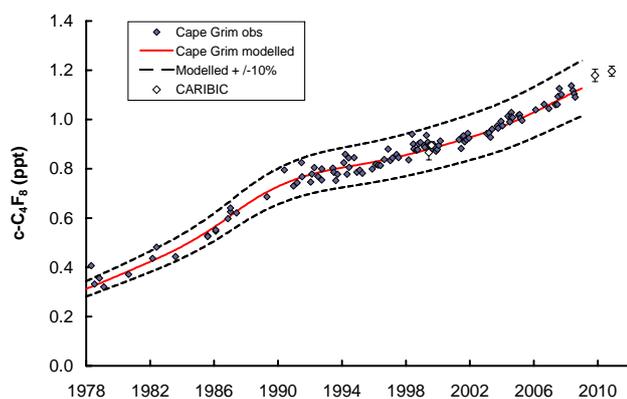
Finally 99 samples, collected during several northern hemispheric flights of the high altitude M55 Geophysica research aircraft during October–November 2009 and January 2010, have also been analysed for their  $c\text{-C}_4\text{F}_8$  content. These lower stratospheric samples (10–20 km altitude) were collected in 2.5 l, electropolished stainless steel canisters at a pressure of 3–4 bar and analysed with the GasPro-Autospec Q combination. Two samples were found to be contaminated and were rejected from the subsequent data analysis. Details of the Geophysica sampling system can be found in Kaiser et al. (2006). Again, the lack of variability in the data and excellent agreement with the Cape Grim measurements confirms the reliability of the sampling technique.

## 3 Results

### 3.1 Cape Grim

Figure 1 shows the changing abundance of  $c\text{-C}_4\text{F}_8$  at Cape Grim over the period 1978–2008. Background levels have increased from around 0.35 ppt in 1978 to around 1.1 pptv in mid-2008. The growth rate of  $c\text{-C}_4\text{F}_8$  has fluctuated over this 30 yr period, slowing considerably during the late 1980s, but increasing again since  $\sim 2002$ . A linear fit through the 2003–2008 data ( $R^2 = 0.91$ ) yields a growth rate of  $0.030 \pm 0.002$  ppt  $\text{yr}^{-1}$ , or 2.7 %  $\text{yr}^{-1}$  based on the mean 2008 mixing ratio of 1.12 ppt. This is significantly higher than the  $0.016 \pm 0.001$  ppt  $\text{yr}^{-1}$  seen between 1990 and 2002 (linear fit,  $R^2 = 0.81$ ).

In absolute terms the Cape Grim data compares well with recently reported values from the Northern Hemisphere.



**Fig. 1.** Measured and modelled  $c\text{-C}_4\text{F}_8$  in the Southern Hemisphere over the period 1978–2010. Blue diamonds are individual samples collected at Cape Grim, Tasmania ( $41^\circ\text{S}$ ); open diamonds are mean mole fractions (with  $\pm 1\sigma$ ) from CARIBIC flights in 1998, 2009 and 2010. The 1998 CARIBIC samples are from the Northern Hemisphere and have been shifted by +1 yr to allow for interhemispheric mixing. The 2009 and 2010 CARIBIC data are southern hemispheric samples only. For clarity the uncertainty of the individual Cape Grim data points (mean precision = 0.8%) have been omitted. The red line represents the model-derived mole fractions, with the dashed lines showing the effect of a  $\pm 10\%$  change on the modelled emissions.

Saito et al. (2010) reported a mean baseline mixing ratio of 1.22 pptv at Cape Ochiishi ( $43.1^\circ\text{N}$ ,  $145.3^\circ\text{E}$ ) for the period August 2006–September 2009, and a slightly higher mean of 1.33 pptv at Hateruma Island ( $24.1^\circ\text{N}$ ,  $123.8^\circ\text{E}$ ), a site more impacted by emissions from East Asia. However, the reported growth rates of  $0.01\text{ pptv yr}^{-1}$  and  $0.02\text{ pptv yr}^{-1}$  for Ochiishi and Hateruma respectively are significantly lower than those measured at Cape Grim. It should be noted that the Saito et al. measurements are reported on a volume mixing ratio scale, although any correction for non-ideal gas behaviour is likely to be quite small and will not account for the observed difference in growth rates.

### 3.2 Global emission estimates

We use the long-term  $c\text{-C}_4\text{F}_8$  dataset from Cape Grim to derive top-down emission estimates by means of a 2-D global chemistry-transport model. The model grid is divided into 24 equal area, zonally-averaged bands and has 12 vertical layers of 2 km depth. The model has been described elsewhere (Hough, 1989, 1991) and has recently been used to study the temporal behaviour and global distribution of halons (Fraser et al., 1999; Reeves et al., 2005) and HFC-227ea (Laube et al., 2010a). The latitudinal distribution of emissions is based on a function of industrial activity such that 95% of emissions are in the Northern Hemisphere, primarily from mid-latitudes (Reeves et al., 2005). Under these conditions the model's transport scheme has been shown to reproduce the observed global distributions of CFC-11 and

CFC-12 (Reeves et al., 2005). For  $c\text{-C}_4\text{F}_8$ , using an atmospheric lifetime of 3200 yr (Forster et al., 2007), the emissions into the model were varied until the predicted concentrations matched the Cape Grim observations.

The model was initialised with a Cape Grim starting mixing ratio of 0.275 ppt and annual emissions into the model began in 1976. It is important to note that emissions into the mid-latitudes of the Northern Hemisphere will take about 1 yr to impact on observed mixing ratios in the Southern Hemisphere. The emission scenario shown in Fig. 2 is the one that made the modelled mixing ratios closely follow the Cape Grim measurements (Fig. 1, red line). The cumulative emissions required to generate an initial 0.275 ppt at Cape Grim were 9.3 Gg. The model-derived emissions were around  $0.9\text{ Gg yr}^{-1}$  in 1978 and grew steadily during the early 1980s reaching a maximum rate of  $1.7\text{ Gg yr}^{-1}$  in 1986. After 1987, the inferred emissions of  $c\text{-C}_4\text{F}_8$  had to decline rapidly in order to match the decline in growth seen in the observed mixing ratios at Cape Grim, such that by 1993 they had dropped to just  $0.4\text{ Gg yr}^{-1}$ . After 1994 modelled emissions increased slightly, followed by a more significant increase between 2000 and 2004. The most recent observations (2005–2008) suggest emissions may have levelled off at around  $1.1\text{ Gg yr}^{-1}$ . The model-derived mixing ratio of  $c\text{-C}_4\text{F}_8$  in the latitudinal band of Cape Ochiishi ( $43.1^\circ\text{N}$ ) for mid-2008 is 1.22 ppt, which compares well with the 2006–2009 average of 1.22 pptv reported by Saito et al. (2010).

Cumulative global emissions of  $c\text{-C}_4\text{F}_8$  up until the end of 2007 are calculated to be 38.1 Gg, which is equivalent to a 100 yr GWP-weighted emission of 0.39 billion tonnes of  $\text{CO}_2$  (0.39 Pg). Also shown in Fig. 1 are the predicted mixing ratios at Cape Grim derived from a +10% and –10% change in the input emissions. Clearly the majority of measurements lie well within these boundaries.

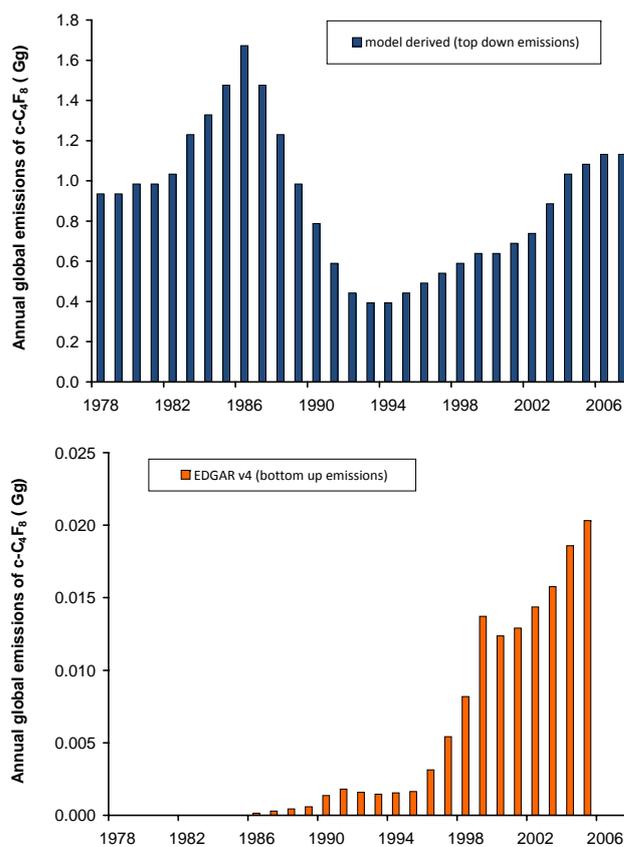
It is possible to compare the model-derived emissions with those published on the EDGAR v4.1 database (EDGAR, 2009). EDGAR emissions are derived from figures reported by individual producers and from national inventories submitted to the UNFCCC (United Nations Framework Convention on Climate Change) by countries that are party to the Kyoto Protocol. EDGAR emissions are available for the period 1986–2005 and are also shown in Fig. 2. Reported emissions have clearly increased over this period, particularly since 1995, but the magnitude of these emissions is well below those derived here from observations, suggesting a large missing source of  $c\text{-C}_4\text{F}_8$ . Cumulative emissions between 1986 and 2005 from EDGAR amount to 0.14 Gg, which is less than 1% of the 15.7 Gg derived from the Cape Grim measurements over the same period. Based on measurements at Cape Ochiishi and Hateruma Island between 2006 and 2009, Saito et al. (2010) estimated  $c\text{-C}_4\text{F}_8$  emissions from East Asia to be  $0.56\text{ Gg yr}^{-1}$ , with China being responsible for around 70% of the total. Global emissions over the same period were estimated to be  $0.6 \pm 0.2\text{ Gg yr}^{-1}$ , implying that the East Asia region (China, Japan, North

Korea, South Korea and Taiwan) is responsible for  $\sim 93\%$  of global emissions. The global emission estimates of Saito et al. (2010) are somewhat lower than those derived from the Cape Grim data for the same period ( $1.1 \text{ Gg yr}^{-1}$ ). This can be largely explained by the fact that the Saito et al. estimates were based on observed growth rates of between  $0.01$  and  $0.02 \text{ ppt yr}^{-1}$ , which are lower than the Cape Grim trend of  $0.030 \pm 0.002 \text{ ppt yr}^{-1}$ . However, if our estimated global emissions are correct it would imply that emissions from China and East Asia are only responsible for around  $50\%$ , which is closer to the figure of  $\sim 30\%$  which was reported by EDGAR v4 (China, Korea, Japan, Taiwan) for the year 2005.

From the observed trend at Cape Grim and the corresponding model-derived emission scenario, it is evident that emissions of  $c\text{-C}_4\text{F}_8$  have varied considerably over the past 30 yr. Indeed, the behaviour of  $c\text{-C}_4\text{F}_8$  is rather unusual when compared to the behaviour of other halocarbons. The decline seen between 1986 and 1993 is difficult to explain. It precedes the similar decline seen in CFC emissions by several years (CFC-11 and 12 emissions peaked in 1988, CFC-113 in 1989), although there is no reason to expect a link between CFC production and  $c\text{-C}_4\text{F}_8$  emissions, and  $c\text{-C}_4\text{F}_8$  is not controlled by the Montreal Protocol.

It is possible that  $c\text{-C}_4\text{F}_8$  is released along with  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  during the production of aluminium although, to the best of our knowledge,  $c\text{-C}_4\text{F}_8$  has not been reported in studies of emissions from the aluminium industry. Furthermore the trends in  $c\text{-C}_4\text{F}_8$  emissions do not necessarily match well those of  $\text{CF}_4$ . From long term tropospheric measurements in both hemispheres Mühle et al. (2010) derived an emission scenario that saw  $\text{CF}_4$  emissions peak in 1980 before declining gradually during the 1980s and then more rapidly after 1990. From the modelling study reported here, emissions of  $c\text{-C}_4\text{F}_8$  increased during the early 1980s reaching a peak in 1986 before a fairly rapid decline between 1987 and 1993.

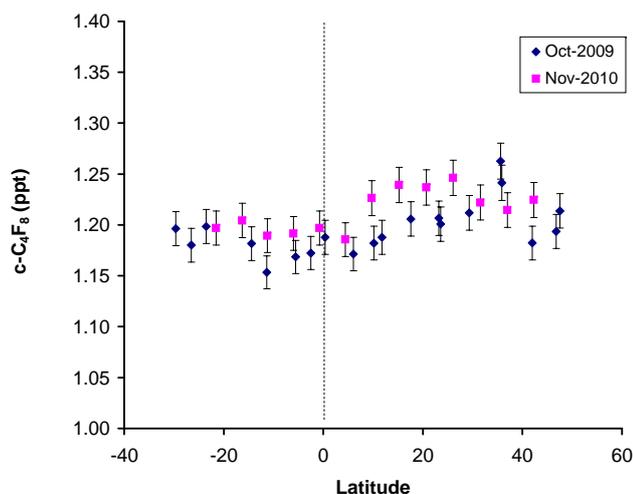
Known uses of  $c\text{-C}_4\text{F}_8$  include the semiconductor industry, for example in plasma etching and chamber cleaning, and also in the production of optical fibres. It has also found some use in refrigerant blends (e.g. R405a) and in fire extinguishers and aerosol sprays.  $c\text{-C}_4\text{F}_8$  has also been used as a tracer in tracer release experiments, although it is highly unlikely to have been used in significantly large quantities.  $c\text{-C}_4\text{F}_8$  can be formed by the dimerisation of tetrafluoroethene ( $\text{C}_2\text{F}_4$ ; Harnisch, 2000) and consequently could be released as a by-product during the manufacture of fluoropolymers. It has also been suggested that the combustion or thermal desorption of polytetrafluoroethene (PTFE) and other fluoropolymers could account for some of the  $c\text{-C}_4\text{F}_8$  found in the atmosphere (Morisaki, 1978; Harnisch, 2000). Finally, a significant natural source of  $c\text{-C}_4\text{F}_8$  can be ruled out as our own recent measurements in deep polar snow (firn air) show no detectable  $c\text{-C}_4\text{F}_8$  in air representative of the atmosphere in the 1940s (Mani, 2010).



**Fig. 2.** Annual global emission estimates for  $c\text{-C}_4\text{F}_8$  derived from a 2-D model fit to the Cape Grim measurements (upper panel) and from the EDGAR v4.1 database (lower panel).

### 3.3 Upper tropospheric measurements

Information on the latitudinal distribution of  $c\text{-C}_4\text{F}_8$  can be obtained from a selection of samples collected during recent CARIBIC flights between Germany (Frankfurt) and South Africa. Figure 3 shows the measurements from flights carried out in October 2009 (to Cape Town) and November 2010 (to Johannesburg). The flight routes were essentially north to south, being confined to the longitude range  $5^\circ\text{--}30^\circ \text{ E}$ . With the exception of the most northerly sample in November 2010 (altitude 8.6 km), all samples were collected at altitudes between 10 and 12 km (250–200 hPa). Based on measured ozone and model-derived potential vorticity ( $\text{O}_3 < 100 \text{ ppb}$ ,  $\text{PV} < 3$ ), none of the samples were significantly affected by mixing with stratospheric air, so are representative of mid-upper tropospheric air. Back trajectories show that, with the exception of samples collected in the region of the ITCZ, the intercepted air in both hemispheres is typically westerly, originating over the Atlantic and beyond. Both flights reveal a small interhemispheric ratio, with mean concentrations higher in the Northern Hemisphere by 2.1% and 1.5% in 2009 and 2010 respectively. This



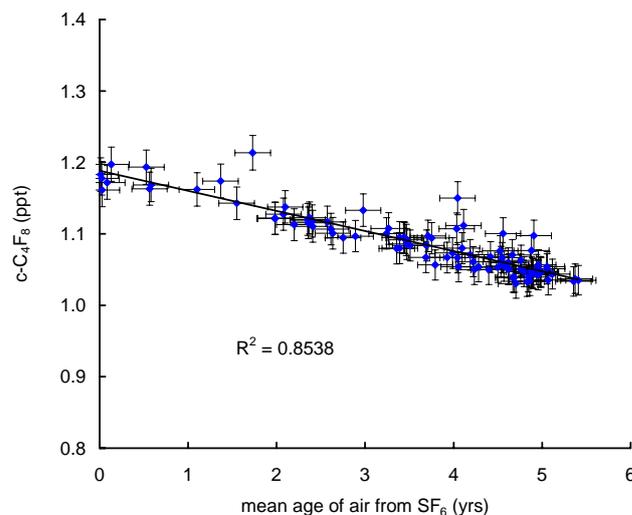
**Fig. 3.** Measurements of  $c\text{-C}_4\text{F}_8$  from CARIBIC flights at 10–12 km altitude between Germany and South Africa in October 2009 and November 2010. Error bars show the mean analytical precision ( $1\sigma$ ).

is consistent with continuing moderate emissions of a long-lived compound primarily from mid-latitudes of the Northern Hemisphere. The mean southern hemispheric concentrations of  $1.18 \pm 0.02$  ppt and  $1.20 \pm 0.01$  ppt in October 2009 and November 2010 show how  $c\text{-C}_4\text{F}_8$  has continued to grow since the end of the Cape Grim record in June 2008 (see Fig. 1). The mean NH concentrations of  $1.20 \pm 0.02$  ppt (October 2009) and  $1.22 \pm 0.02$  ppt (November 2010) are in reasonable agreement with the 2006–2009 average of 1.22 reported by Saito et al. (2010) at Cape Ochiishi.

Samples from two earlier CARIBIC flights have also been analysed for  $c\text{-C}_4\text{F}_8$ . These flights took place in June and August 1998 between Germany and Sri Lanka, meaning that all samples were collected in the Northern Hemisphere over a geographical range of  $10\text{--}50^\circ\text{N}$  and  $10\text{--}75^\circ\text{E}$ , and an altitude range of 9–11 km. The mean concentrations were  $0.87 \pm 0.03$  ppt and  $0.90 \pm 0.01$  ppt in June (9 samples) and August (11) respectively. These values are consistent with the Cape Grim observations and have been included in Fig. 1, with a time shift of +1 yr to allow for interhemispheric exchange.

### 3.4 Lower stratospheric measurements

The recent growth rate of  $c\text{-C}_4\text{F}_8$  in the atmosphere is further confirmed from measurements using the Geophysica high altitude research aircraft. Samples were collected in the upper troposphere and lower stratosphere (UT/LS) during two flights at mid-latitudes from Oberpfaffenhofen, Germany on 30 October and 4 November 2009, and eight flights at high latitudes from Kiruna, Sweden between 22 January and 2 February 2010. The samples were all collected in the Northern Hemisphere, over an altitude range of 9–20 km, with



**Fig. 4.** Lower stratospheric measurements of  $c\text{-C}_4\text{F}_8$  from Geophysica flights in the Northern Hemisphere between October 2009 and January 2010 plotted against mean age of air. y-axis error bars show the mean analytical precision ( $1\sigma$ ) and the x-axis error bars represent the mean ( $1\sigma$ ) uncertainty in the age calculation from measured  $\text{SF}_6$ .

a geographical range of  $48\text{--}53^\circ\text{N}$ ,  $7\text{--}12^\circ\text{E}$  (Oberpfaffenhofen) and  $66\text{--}76^\circ\text{N}$ ,  $1^\circ\text{W}\text{--}28^\circ\text{E}$  (Kiruna).

It is well known that long-lived compounds form compact relationships in the lower stratosphere (Plumb and Ko, 1992) and, consequently, it is possible to date a lower stratospheric air sample in terms of an age since stratospheric entry, (i.e. the mean stratospheric transport time of a given air parcel) by using a long-lived tracer which is growing in the atmosphere at a well defined rate. As recently described by Laube et al. (2010b), the approach of Engel et al. (2002) has been used to derive mean ages of the Geophysica samples based on concurrent measurements of  $\text{SF}_6$ . The tropospheric trend of  $\text{SF}_6$  was taken from the NOAA-ESRL records which were obtained from <http://www.esrl.noaa.gov/gmd/> (updated from Geller et al., 1997). The plot of  $c\text{-C}_4\text{F}_8$  against mean age (Fig. 4) shows a well defined decrease in mixing ratio with mean age confirming the positive growth of  $c\text{-C}_4\text{F}_8$  over the past 5–6 yr. A linear fit to the data ( $R^2 = 0.854$ ) yields a mean growth rate of  $0.028 \pm 0.001$  ppt  $\text{yr}^{-1}$ , which is similar to the southern hemispheric growth rate of  $0.030 \pm 0.002$  ppt  $\text{yr}^{-1}$  derived from the Cape Grim record (2003–2008). This also confirms the very long lifetime of  $c\text{-C}_4\text{F}_8$  as there is no evidence for a significant sink reaction in the lower stratosphere. The mean upper tropospheric concentration of  $1.18 \pm 0.02$  ppt (derived from samples with mean age less than 0.15 yr) is similar to the CARIBIC northern hemispheric means of  $1.20 \pm 0.02$  ppt and  $1.22 \pm 0.02$  ppt in October 2009 and November 2010 respectively.

#### 4 Summary and conclusions

Long-term observations from Cape Grim together with recent aircraft measurements in the upper troposphere and lower stratosphere reveal the continuing accumulation of  $c\text{-C}_4\text{F}_8$  in the remote atmosphere. The current (2010) abundance of  $c\text{-C}_4\text{F}_8$  is  $\sim 1.2$  ppt and is growing at  $0.03$  ppt  $\text{yr}^{-1}$ . Model calculations suggest that global emissions of  $c\text{-C}_4\text{F}_8$  have increased in recent years after a steady decline in the late 1980s and early 1990s. Current emission rates are estimated to be of the order of  $1.1$  Gg  $\text{yr}^{-1}$ . Cumulative emissions up to and including 2007 are 38.1 Gg, which is equivalent to a 100 yr GWP-weighted emission of 0.39 billion tonnes of  $\text{CO}_2$ . To put this in context, it is similar to the total annual anthropogenic emissions of  $\text{CO}_2$  from the UK (0.47 billion tonnes in 2009; DECC, 2011). Comparison with bottom up emissions from the EDGAR v4 database reveals a large discrepancy, with reported emissions accounting for less than 1 % of those required to match the Cape Grim measurements. There is clearly a large missing, or unreported, source of this potent greenhouse gas, and it has been speculated that this could be from the manufacture or incineration of fluoropolymers such as PTFE. Further research is required to identify this missing source of  $c\text{-C}_4\text{F}_8$  so that accurate data can be reported to the UNFCCC and other relevant agencies.

*Acknowledgements.* The UEA Cape Grim and CARIBIC programmes are currently supported by the UK NERC National Centre for Atmospheric Science. The Cape Grim programme has previously received funding from the former UK Government Department of Environment (GA/4/2/57). The CARIBIC programme has previously received funding from UK NERC (NER/T/S/2000/01040 and GST/02/2218) and the European Union (EVK2-GT2001-00101). Further funding came from NERC award NE/F021194/1). The Geophysica flights were funded by the European Space Agency, the Forschungszentrum Jülich and the EU RECONCILE project (226365-FP7-2008-1). F. Mani acknowledges an EU Marie Curie studentship (MEST-CT-2004-514159). J. Laube is funded by a UK NERC Fellowship (NE/F015585/1). We are indebted to G. Mills, P. Begley and S. Humphrey for technical support and would like to thank the CARIBIC and Geophysica teams and those at CSIRO involved in the long-term operation of the Cape Grim station.

Edited by: J. B. Burkholder

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