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Distributions, long term trends and emissions of four perfluorocarbons in remote parts of the atmosphere and firn air

J. C. Laube[1], **C. Hogan**[1], **M. J. Newland**[1], **F. S. Mani**[1,2], **P. J. Fraser**[3], **C. A. M. Brenninkmeijer**[4], **P. Martinerie**[5], **D. E. Oram**[6], **T. Röckmann**[7], **J. Schwander**[8], **E. Witrant**[9], **G. P. Mills**[1], **C. E. Reeves**[1], **and W. T. Sturges**[1]

[1]School of Environmental Sciences, University of East Anglia, Norwich, UK
[2]School of Applied Sciences, Fiji National University, Suva, Fiji
[3]Centre for Australian Weather and Climate Research, Commonwealth Scientific and Industrial Research Organisation, Aspendale, Victoria 3195, Australia
[4]Max Planck Institute for Chemistry, Air Chemistry Division, Mainz, Germany
[5]UJF – Grenoble 1/CNRS, Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) UMR5183, Grenoble, 38041, France
[6]National Centre for Atmospheric Science, School of Environmental Sciences, University of East Anglia, Norwich, UK
[7]Institute for Marine and Atmospheric Research, Utrecht University, Utrecht, The Netherlands
[8]Physics Institute, University of Berne, Bern, Switzerland
[9]UJF – Grenoble1/CNRS, Grenoble Image Parole Signal Automatique (GIPSA-lab), UMR5216, B.P. 46, 38402 St. Martin d'Hères, France

Correspondence to: J. C. Laube (j.laube@uea.ac.uk)

Abstract. We report the first data set of atmospheric abundances for the following four perfluoroalkanes: n-decafluorobutane ($n\text{-}C_4F_{10}$), n-dodecafluoropentane ($n\text{-}C_5F_{12}$), n-tetradecafluorohexane ($n\text{-}C_6F_{14}$) and n-hexadecafluoroheptane ($n\text{-}C_7F_{16}$). All four compounds could be detected and quantified in air samples from remote locations in the Southern Hemisphere (at Cape Grim, Tasmania, archived samples dating back to 1978) and the upper troposphere (a passenger aircraft flying from Germany to South Africa). Further observations originate from air samples extracted from deep firn in Greenland and allow trends of atmospheric abundances in the earlier 20th century to be inferred. All four compounds were not present in the atmosphere prior to the 1960s. $n\text{-}C_4F_{10}$ and $n\text{-}C_5F_{12}$ were also measured in samples collected in the stratosphere with the data indicating that they have no significant sinks in this region. Emissions were inferred from these observations and found to be comparable with emissions from the EDGAR database for $n\text{-}C_6F_{14}$. However, emissions of $n\text{-}C_4F_{10}$, $n\text{-}C_5F_{12}$ and $n\text{-}C_7F_{16}$ were found to differ by up to five orders of magnitude between our approach and the database.

Although the abundances of the four perfluorocarbons reported here are currently small (less than 0.3 parts per trillion) they have strong Global Warming Potentials several thousand times higher than carbon dioxide (on a 100-yr time horizon) and continue to increase in the atmosphere. We estimate that the sum of their cumulative emissions reached 325 million metric tonnes CO_2 equivalent at the end of 2009.

1 Introduction

Perfluorocarbons (PFCs) are fully fluorinated hydrocarbons which have very long atmospheric lifetimes and very high Global Warming Potentials (GWPs) in the case of alkanes (IPCC, 2007; Bravo et al., 2010). Abundances of four major PFCs have been reported in the atmosphere so far: tetrafluoromethane (CF_4), hexafluoroethane (C_2F_6), n-octafluoropropane (C_3F_8) and cyclo-octafluorobutane (c-C_4F_8) (e.g. Rasmussen et al., 1979; Penkett et al., 1981; Sturges et al., 1999; Khalil et al., 2003; Culbertson et al., 2004; Worton et al., 2007; Mühle et al., 2010; Saito et al.,

2010; Oram et al., 2012). The atmospheric sources of these previously reported compounds are entirely industrial and mainly attributed release from aluminium production, electronics manufacturing, fire protection and solvent applications (IPCC/TEAP, 2005; Mühle et al., 2010), except for CF_4 which has been found to have been present in the atmosphere in pre-industrial times (e.g. Harnisch et al., 1996a; Worton et al., 2007). Emissions and usage have also been reported for other perfluoroalkanes such as n-C_4F_{10} and n-C_5F_{12}. These have been proposed and/or used as refrigerants, in air conditioning, as fire suppressants and in semiconductor manufacturing (Robin and Iikubo, 1992; Mazurin et al., 1994; IPCC/TEAP, 2005; EDGAR, 2010). In addition n-C_6F_{14} and n-C_7F_{16} have been reported as solvents and heat transfer fluids (Stone & Springer, 1995; EPA, 2006; EDGAR, 2010; Waugh et al., 2011). The GWPs of three of the latter four compounds are 8860 (n-C_4F_{10}), 9160 (n-C_5F_{12}) and 9,300 (n-C_6F_{14}) on a 100-yr time horizon (IPCC, 2007). Thus it is likely that the GWP of n-C_7F_{16} is also between 8000 and 10 000. In addition these compounds have very long atmospheric lifetimes of 2,600 (n-C_4F_{10}), 4100 (n-C_5F_{12}), 3,100 (n-C_6F_{14}) and 3000 (n-C_7F_{16}) years (WMO, 2011). Thus even comparably small emissions can result in significant and long-lasting effects on atmospheric radiative forcing. This work aims to fill the gap in current understanding by providing temporal and spatial distributions of atmospheric abundances for n-C_4F_{10}, n-C_5F_{12}, n-C_6F_{14} and n-C_7F_{16}. Finally it is notable that a work with a similar scope appeared in Atmos. Chem. Phys. Discuss. on the same day as ours (Ivy et al., 2012).

2 Experimental methods

The data reported here are based on Gas Chromatography-Mass Spectrometry (GC-MS) measurements of air samples using a system that has been described in detail in Laube et al., 2010a. Calibration scales were established by diluting the pure compounds down to parts per trillion (ppt) mixing ratio levels with a static dilution system also described in Laube et al. (2010a). In case of n-C_6F_{14} and n-C_7F_{16} this system had to be slightly modified as these compounds are liquid at room temperature. More details on instruments, linearity, identification and calibration can be found in the supplementary information. Air samples were collected as follows:

1. From an air archive collected at a ground-based observatory at Cape Grim, Tasmania (41° S, 145° E, subsamples of the original Cape Grim air archive up to 1994, samples collected directly for UEA since then). These samples have been shown to contain concentrations of atmospheric trace gases that are representative of the remote and well-mixed southern hemispheric troposphere.

2. On board a Lufthansa aircraft at cruising altitudes of 8.6 to 12.2 km between Frankfurt (Main), Germany and Cape Town, South Africa on 27 and 28 October 2009 and on 20 March 2011, as well as one flight from Frankfurt to Johannesburg, South Africa on 14 November 2010 (CARIBIC project, www.caribic-atmospheric. com, 48 samples analysed for this work).

3. From deep firn air (22 samples) in Greenland at 77.445° N, 51.066° W and 2484 m a.s.l. in July 2008 (the North Greenland Eemian Ice Drilling project; NEEM).

4. In the mid- and high-latitudinal upper troposphere and stratosphere (9 to 20 km) on board the M55 Geophysica high altitude aircraft during two flights from and returning to Oberpfaffenhofen, Germany on 30th October and 4th November 2009 (48–54° N, 7–12° E) and seven flights from and returning to Kiruna, Sweden between 22nd January and 2nd February 2010 (66–77° N, 1° W–29° E).

Further details on sample collection can be found in Fraser et al. (1999), Oram et al. (2012) (Cape Grim), Brenninkmeijer et al. (2007) (CARIBIC), Buizert et al. (2011) (NEEM) and Kaiser et al. (2006) (Geophysica).

3 Results and discussion

3.1 Long-term tropospheric trends from Cape Grim, Tasmania and firn air

3.1.1 n-C_4F_{10} and n-C_5F_{12}

Figure 1 shows the long term atmospheric trend of n-C_4F_{10} from 39 samples collected at the Cape Grim station. This archive has been shown to represent unpolluted southern hemispheric (SH) abundances for a large variety of trace gases, by comparison of archive data with in situ Cape Grim data over extended periods (CFCs: 1978–present; HCFCs, HFCs, halons: 1998–present; PFCs: 2004–present; e.g. Oram et al., 1996; Fraser et al., 1999; Mühle et al., 2010; Vollmer et al., 2011). The compound was already present in the southern hemispheric atmosphere in 1978 and its abundances have been increasing ever since. This is the case for all four compounds reported here. n-C_4F_{10} mixing ratios increased from 0.018 ± 0.002 ppt in 1978 to 0.171 ± 0.002 ppt at the end of 2010. Growth rates were inferred by fitting a five parameter sigmoid expression to the data set (also shown in Fig. 1) similar to the method presented in Sturges et al., 2012. We estimate growth rates increasing from 4.1 part per quadrillion (ppq) per year in 1979 to a maximum of 6.7 ppq yr^{-1} in 1996. Since then growth rates have been decreasing to 3.5 ppq yr^{-1} in 2005 reaching 2.6 ppq yr^{-1} in 2010. All annual growth rates can be found in the supplementary information.
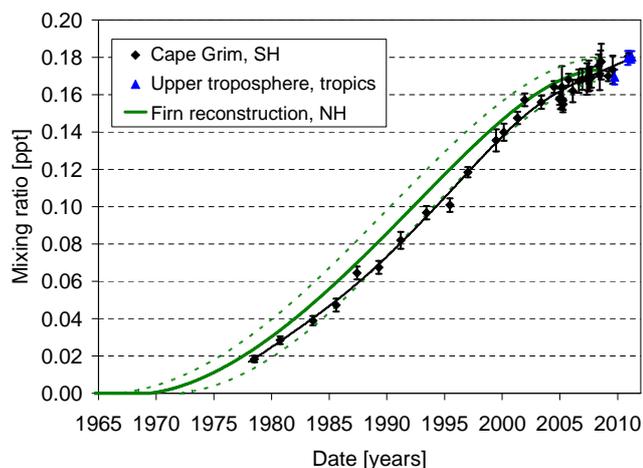
Fig. 1. Mixing ratios of n-C_4F_{10} as a function of time as measured in air samples collected in the Southern Hemisphere (black diamonds, from Cape Grim, Tasmania, 41° S, 145° E) as well as derived from Northern Hemispheric deep firn air samples (green line, collected in Greenland in 2008, 77.445° N, 51.066 ° W, 2484 m a.s.l.). The black line is a sigmoid expression fitted through the Cape Grim trend in order to derive growth rates and emissions. The blue triangles are mixing ratio averages of samples collected in the tropical troposphere between 10 and 12 km and within 20° N and 20° S. The error bars on the blue triangles and the black diamonds represent the 1σ measurement standard deviations. The dashed lines consist of the sum of **(a)** the firn air model maximum and minimum runs obtained by adding and subtracting the 1σ measurement standard deviations to/from the firn data and **(b)** the maximum deviation of the actual mixing ratios from the polynomial fitted to derive the NH trend.

The northern hemispheric (NH) trend of n-C_4F_{10} was inferred from the firn air measurements. Firn provides a natural air archive for all compounds that are sufficiently inert in this environment, which is a reasonable assumption for compounds as stable as perfluoroalkanes (see also Worton et al., 2007). Firn air has been previously used to reconstruct the long term atmospheric trends of a variety of atmospheric trace gases (e.g. Butler et al., 1999; Sturges et al., 2001; Montzka et al., 2004; Worton et al., 2007; Martinerie et al., 2009 or Laube et al., 2010a). We use here an iterative modelling approach to convert the measured mixing ratios and firn depth profiles into atmospheric trends (Trudinger et al., 2002) in conjunction with a firn physical transport model (Witrant et al., 2011) which accounts for gaseous diffusion, gravitational settling, downward advection and bubble trapping within the firn. The model has been tuned to the NEEM site according to the data set provided by Buizert et al. (2011). This method requires essentially no presumptions about the atmospheric trends, other than compounds increasing monotonically from negligible abundances to the known present day mixing ratios. A comparison of measured firn depth profiles to firn model results can be found in the supplementary information.
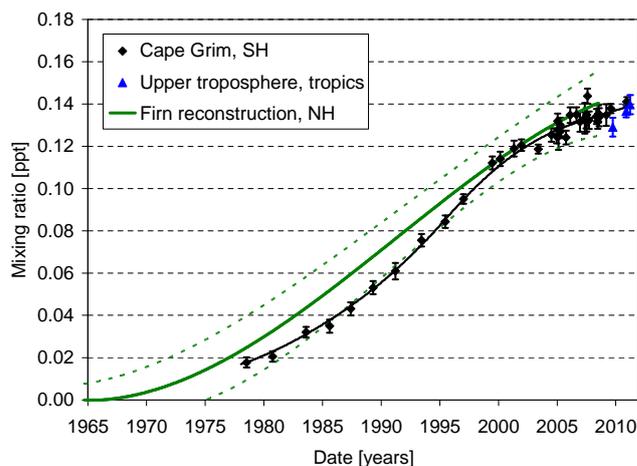

Fig. 2. Same as in Fig. 1 but for n-C_5F_{12}.

As can be seen in Fig. 1 the NH trend extends further back in time compared to the SH archive with n-C_4F_{10} establishing a presence in the atmosphere between the late 1960s and early 1970s with mixing ratios of less than our detection limit of 1 ppq prior to this time. n-C_4F_{10} has been slightly more abundant in the NH than in the SH which would be expected for an anthropogenic compound with increasing concentrations and main sources in the industrialised countries of the NH. The temporal evolution of the trend is consistent with this hypothesis as the increase and the recent decline in growth is detected in both hemispheres (Fig. 1). The uncertainties connected with the firn reconstruction do not allow further interpretation. The firn air trend ends in mid 2008 i.e. the time of the respective field campaign. It should be noted, however, that the uppermost part of the firn contains air which does less well represent the averaged composition of the atmosphere. Therefore a direct comparison with the Cape Grim trend should only be considered appropriate until 2007.

A similar compilation of results is shown in Fig. 2 for n-C_5F_{12}. Mixing ratios at Cape Grim increased monotonically from 0.018±0.002 ppt in 1978 to 0.141±0.002 ppt at the end of 2010. Generally n-C_5F_{12} shows similarities to n-C_4F_{10} at Cape Grim with a very constant abundance ratio of 0.79±0.04 (n-C_5F_{12}/n-C_4F_{10}) for almost the complete data set (except the very low abundances observed in 1978 which also have higher relative uncertainties). Consequently growth rates show a similar behaviour increasing from 2.1 ppq yr^{-1} in 1979 to 6.1 ppq yr^{-1} in 1996 and then decreasing to 2.4 ppq yr^{-1} in 2005 and 1.6 ppq yr^{-1} in 2010. The trend derived from the firn air again implies that detectable abundances of n-C_5F_{12} appeared in the atmosphere between the late 1960s and early 1970s. Due to worse measurement precisions the uncertainties of this firn trend are greater compared to that of n-C_4F_{10} but the reconstruction generally follows the Cape Grim trend at

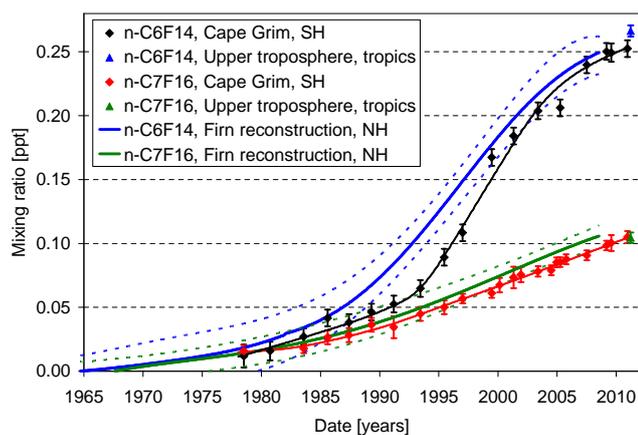**Fig. 3.** Same as in Fig. 1 but for n-C_6F_{14} (black and blue) and n-C_7F_{16} (red and green).

comparable abundances. In the 1990s NH and SH mixing ratios of n-C_5F_{12} begin to increase less rapidly until the end of the firn record in 2008. Possible explanations for this behaviour could be the declining emissions which are explained in more detail in Sect. 3.3. Of the four compounds reported here n-C_5F_{12} is the one with the smallest growth rates in recent years. However, it should be noted that mixing ratios of n-C_5F_{12} have increased by more than 30 % in both hemispheres over this slowdown period (1996-2008). We have also compared our SH mixing ratios at the end of 2010 to the 2011 globally averaged background atmospheric mole fractions reported in the simultaneously published work of Ivy et al., 2012. They find comparable mixing ratios of 0.18 ppt for C_4F_{10} (our value: 0.171 ppt) and 0.12 ppt for C_5F_{12} (our value: 0.141 ppt). However, in addition to possible calibration scale differences, the limitations of this comparison due to the above mentioned differences in collection dates and averaging methods should be noted.

3.1.2　n-C_6F_{14} and n-C_7F_{16}

For procedural reasons fewer samples were analysed for n-C_6F_{14} and n-C_7F_{16} leading to a reduced data set for these two compounds. Figure 3 shows the respective time series derived from Cape Grim samples with mixing ratios of 0.016 ppt (n-C_6F_{14}) and 0.012 ppt (n-C_7F_{16}) in 1978. Apart from the firn trends indicating an onset of emissions between the late 1960s and early 1970s (similar to n-C_4F_{10} and n-C_5F_{12}) three points are most notable:

1. Of the four compounds reported here n-C_6F_{14} exhibited the highest growth rates ranging from 2.7 ppq yr^{-1} in 1979 to 15.2 ppq yr^{-1} in 1998, more than double the maximum growth rates of n-C_4F_{10} and n-C_5F_{12}. In recent years growth rates of this compound have decreased but were still comparably high with 8.3 ppq yr^{-1} in 2005 and 4.0 ppq/year in 2010. As a con-

sequence n-C_6F_{14} became the most abundant of these four PFCs from 1999 onwards reaching 0.253±0.007 ppt at the end of 2010. Ivy et al., 2012 report a comparable globally averaged mixing ratio of 0.28 ppt for 2011.

2. The trend of n-C_6F_{14} derived from the firn deviates somewhat from the Cape Grim trend during the period when n-C_6F_{14} increased most rapidly in the atmosphere. This is likely caused by the limitations of the firn reconstruction which gives a smoothed view of reality, especially for reconstructions based on a single site with a limited number of data points in deep firn where age mixing is strong. This is most pronounced in the case of n-C_6F_{14} which has the least linear atmospheric trend of the four compounds. To evaluate the limitations of the reconstruction method we also derived atmospheric histories from firn using an inverse modelling approach (LGGE-GIPSA inverse model as described in Witrant et al., 2011 and Wang et al., 2011) which gave similar results within the uncertainties presented in the figures.

3. Growth rates of n-C_7F_{16} at Cape Grim increased from 0.5 ppq/year in 1979 to 3.2 ppq yr^{-1} in 1992. They then stabilised and have been constant at 3.5 ppq yr^{-1} since 2003. Therefore n-C_7F_{16} is the only one of the four compounds which shows no significant decline in growth rate in recent years. However, with a mixing ratio of just over 0.1 ppt (0.105±0.005 ppt at the end of 2010) at Cape Grim it so far remains the least abundant PFC reported here. Again, Ivy et al. (2012) report a comparable globally averaged mixing ratio of 0.12 ppt for 2011.

3.2　Aircraft data from stratosphere and upper troposphere

Stratospheric samples can also be utilised as a short-term air archive in the case of very long-lived atmospheric trace gases with no significant sinks in this region. This has been found previously by Harnisch et al. (1996b) for CF_4 and Oram et al. (2012) for c-C_4F_8. The 99 stratospheric air samples collected on aircraft flights in the mid and high northern hemisphere as described above were analysed for their content of n-C_4F_{10}, n-C_5F_{12} and also SF_6. The latter can be used to infer so-called mean ages of air which represent the average time the sampled stratospheric air parcel has spent in the stratosphere (see details of the method in Engel et al., 2002, its application in Laube et al., 2010b or Oram et al., 2012, and the NOAA-ESRL tropospheric record of SF_6 from Geller et al. (1997) with updates downloaded from http://www.esrl.noaa.gov/gmd/). Vertical transport times in the stratosphere are on the order of years and our data set allows us to track the temporal evolution of n-C_4F_{10} and n-C_5F_{12} up to six years back in time from the dates of the field campaigns in late 2009 and early 2010.
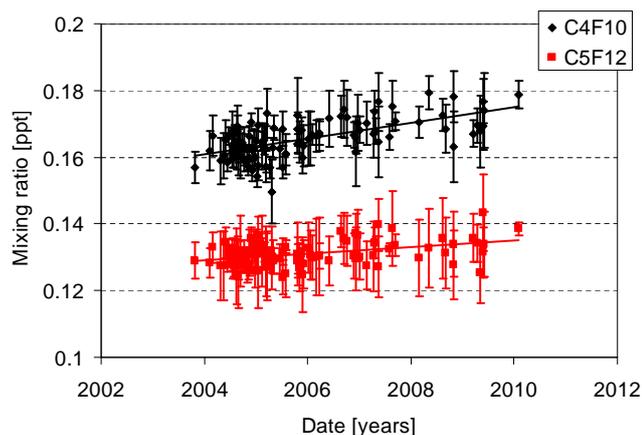
Fig. 4. Mixing ratios of n-C_4F_{10} (black) and n-C_5F_{12} (red) in the stratosphere above Oberpfaffenhofen, Germany in late 2009 and above Kiruna, Sweden in early 2010. Tropospheric equivalent dates were assigned using stratospheric mean ages of air (i.e. average stratospheric transit times) derived from simultaneous measurements of SF_6. The error bars again represent the 1 σ measurement standard deviations.

The results are shown in Fig. 4. It should be noted that analytical precisions for these stratospheric measurements were generally worse compared to the data presented in Sect. 3.1. This is due to limitations during the analysis with limited MS dwell times on the respective ions as other compounds which eluted close in time also needed to be measured. In the upper tropospheric/lower stratospheric region mixing ratios around 0.179 ppt for n-C_4F_{10} and 0.139 ppt for n-C_5F_{12} were observed which is consistent with the tropospheric abundances inferred from ground-based measurements. A linear regression gives average growth rates of 2.3±0.6 ppq yr^{-1} for n-C_4F_{10} and 1.0±0.5 ppq yr^{-1} for n-C_5F_{12} for the period from late 2003 to early 2010 (uncertainties are 2σ standard deviations). These growth rates agree with the average growth rates from Cape Grim measurements within the uncertainties (i.e. 2.9±0.8 ppq for n-C_4F_{10} and 1.9±0.8 ppq yr^{-1} for n-C_5F_{12} averaging from 2004 to 2010 to account for interhemispheric transport). This also indicates that the two compounds do not have any significant sinks in the lower stratosphere as the respective sink reactions would misleadingly lead to higher growth rate estimates. However, it should be noted that there are uncertainties of this technique which we can not account for such as the unknown distribution of ages contained within a stratospheric air parcel.

The upper tropospheric measurements obtained from the CARIBIC samples between 2009 and 2011 are displayed in Figs. 5 (n-C_4F_{10}), 6 (n-C_5F_{12}), and 7 (n-C_6F_{14} and n-C_7F_{16}). All four flights represent essentially hemispheric cross-sections with very little longitudinal variation (within 6 and 28 °E). A full data set is again only available for n-C_4F_{10} and n-C_5F_{12} which will be discussed first. Cape Grim growth rates of n-C_4F_{10} and n-C_5F_{12} were both below 2 %

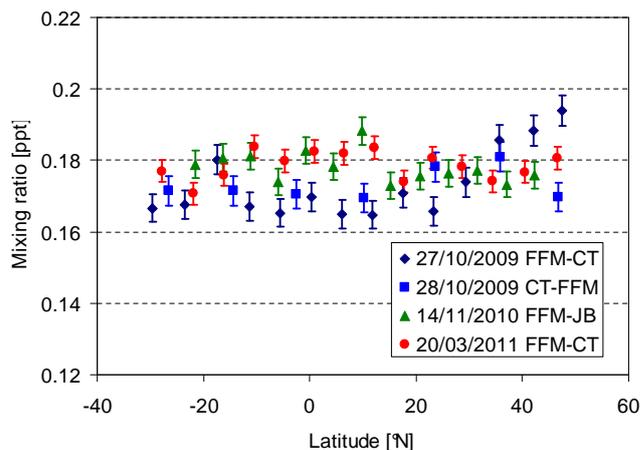**Fig. 5.** Mixing ratios of n-C_4F_{10} as a function of latitude as measured in air samples collected at altitudes between 8.6 and 12.2 km during passenger aircraft flights from Frankfurt (Main, FFM), Germany to Cape Town (CT) and Johannesburg (JB), both South Africa.
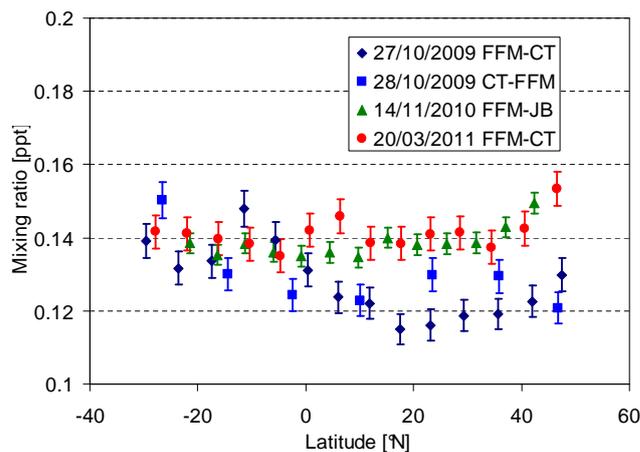

Fig. 6. Same as in Fig. 5 but for n-C_5F_{12}.

in 2010. As the 1σ measurement uncertainties are around 2 % (n-C_4F_{10}) and 3.5 % (n-C_5F_{12}) interhemispheric gradients are not detectable during our measurement period. It should also be noted that individual mid-latitudinal samples might be influenced by stratospheric air resulting in too low abundances. However, the tropical samples (within 20° of the equator) can be considered as most representative for global tropospheric trends as these are unlikely to be influenced by stratospheric air due to the higher tropopause in this region. Thus the respective average mixing ratios are also included in Figs. 1 and 2 and show good agreement with the ground-based samples.

Only the air samples from the most recent CARIBIC flight were analysed for their content of n-C_6F_{14} and n-C_7F_{16} (Fig. 7). n-C_6F_{14} is on average more abundant in the NH which is supported by a tropical average mixing ratio more
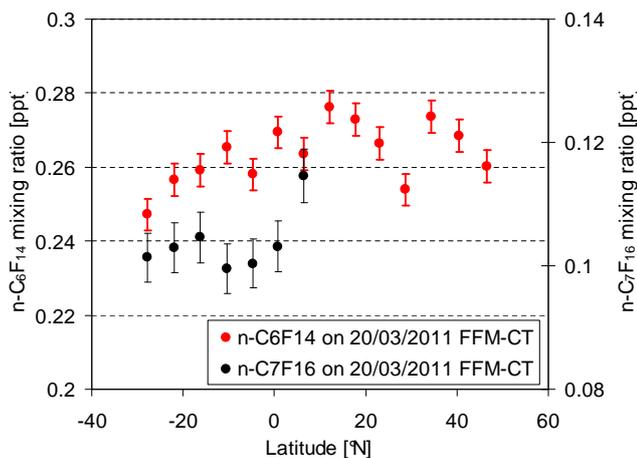
Fig. 7. Same as in Fig. 6 but for n-C_6F_{14} (red) and n-C_7F_{16} (black).

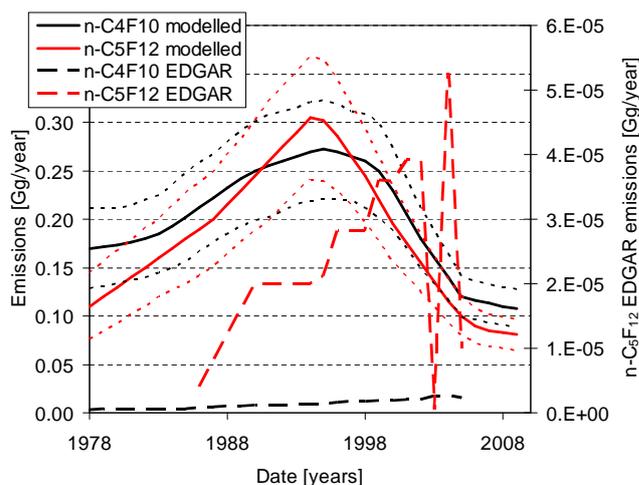**Fig. 8.** Time series of the global emissions of n-C_4F_{10} (black) and n-C_5F_{12} (red) modelled from the Cape Grim trends (solid lines) in gigagrams (Gg) per year as compared to emissions reported by the EDGAR emission database (long-dashed lines, EDGAR, 2010). Please note that the EDGAR emissions for n-C_5F_{12} are very small and thus plotted on a separate y-axis. The short-dashed lines are uncertainty estimates consisting of **(a)** the 1 σ measurement standard deviations plus **(b)** the square root of the sum of the squares of the of the deviation of the actual mixing ratios from the polynomials fitted to derive the growth rates plus **(c)** an additional calibration scale uncertainty (see Supplement).

than 5 % higher than the one observed at Cape Grim less than 4 months earlier. In the case of n-C_7F_{16} data is only available for half of the samples due to an intermittent problem with the MS data acquisition method. Therefore we only compare the tropical average with Cape Grim data and find good agreement within the analytical uncertainties.

3.3 Top-down emission estimates and comparison with EDGAR database

Emissions were estimated using a 2-D atmospheric chemistry-transport model (similar to the method in Laube et al., 2010a and Oram et al., 2012) which has been proven to reproduce well known emissions of long lived compounds emitted mainly in the northern hemisphere when constrained by southern hemispheric observations (Reeves et al., 2005). Emissions were assigned predominantly (i.e. 99 %) to the northern mid-latitudes for all four compounds according to distributions from EDGAR, 2010 (version 4.1). The main loss processes for these compounds occur outside the model domain hence the only sink was a diffusive loss from the top of the model which was adjusted to govern the lifetime of the compounds. But as the lifetimes of these compounds are on the order of several thousand years (IPCC, 2007; WMO, 2011), the sink reactions have a negligible influence on the derived emissions. For the same reasons errors in these lifetimes cannot reconcile any differences between the inventory emissions and those derived from atmospheric data. The model emissions were adjusted so that the modelled mixing ratios for the location of Cape Grim agreed with the sigmoidal trends fitted to the Cape Grim archive measurements. As displayed in Fig. 8 for n-C_4F_{10} and n-C_5F_{12} we find that emissions continuously increased from 1978 (0.17 Gg yr^{-1} for n-C_4F_{10} and 0.11 Gg yr^{-1} for n-C_5F_{12}), peaked in the mid 1990s (0.27 Gg yr^{-1} for n-C_4F_{10} and 0.31 Gg yr^{-1} for n-C_5F_{12}) with a subsequent decline to 0.11 Gg yr^{-1} for n-C_4F_{10} and 0.08 Gg yr^{-1} for n-C_5F_{12}. Please see the sup-

plementary information for the complete numerical annual emissions data set. A comparison with published "bottom-up" industrial emissions as reported in the EDGAR database (EDGAR, 2010) is also shown in Fig. 8 for n-C_4F_{10} and n-C_5F_{12}. In both cases emissions reported in EDGAR are too low by orders of magnitude (about 1–2 in the case of n-C_4F_{10} and 4–5 in the case of n-C_5F_{12}). It is also evident from the comparison that the temporal evolution of emissions does not match those reported in EDGAR. This is not surprising given that there are only a limited number of countries reporting emissions of all four compounds to the EDGAR database. It is particularly true in the case of n-C_5F_{12} where Romania has been the only country reporting emissions to EDGAR, 2010.

In contrast we find reasonable agreement between the emissions of n-C_6F_{14} from both approaches (Fig. 9) with our estimates increasing from 0.16 Gg yr^{-1} in 1978 to 0.88 Gg yr^{-1} in 1997 followed by a decline to 0.23 Gg yr^{-1} in 2009. Finally, for n-C_7F_{16} (also Fig. 9) we find emissions increased from 0.08 Gg yr^{-1} 1978 to 0.23 Gg yr^{-1} in 2001 and stabilising at this rate thereafter. The respective EDGAR emissions are up to 60 % higher between 1990 and 1999 and up to 75 % lower before and after that period – both deviations exceeding our estimated uncertainty envelope of up to ±65 %.
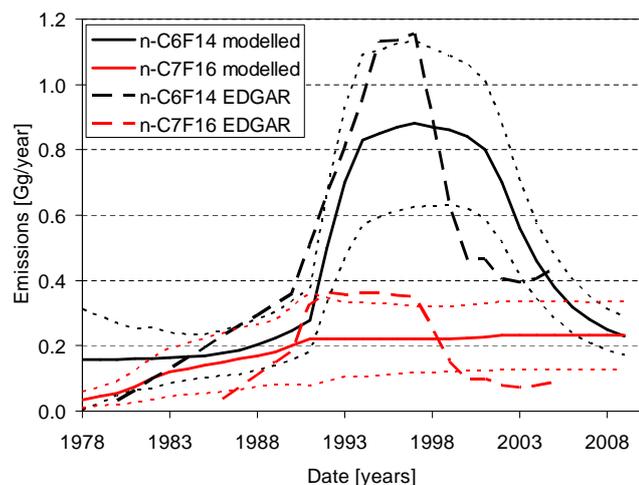
Fig. 9. Same as in Fig. 8 but for n-C$_6$F$_{14}$ (black) and n-C$_7$F$_{16}$ (red).

Fig. 10. Cumulative emissions of C4 to C7 perfluorocarbons: the four compounds reported here plus those of c-C$_4$F$_8$ as updated from Oram et al. (2012) in million metric tonnes of CO$_2$ equivalent. The Global Warming Potentials (GWPs) on a 100-yr time horizon reported in IPCC (2007) were applied to derive these emissions. As no GWP is reported for n-C$_7$F$_{16}$ in IPCC, 2007 and Bravo et al. (2010) we assumed a similar GWP to that of n-C$_6$F$_{14}$.

4 Discussion and conclusions

Four perfluorocarbons, n-C$_4$F$_{10}$, n-C$_5$F$_{12}$, n-C$_6$F$_{14}$ and n-C$_7$F$_{16}$, have been first observed in remote parts of the atmosphere and firn air. These compounds are all very strong greenhouse gases with detectable abundances appearing in the atmosphere between the late 1960s and early 1970s and increasing ever since. A comparison of NH trends derived from firn air with an archived record from Cape Grim, Tasmania showed good agreement except for n-C$_6$F$_{14}$ where the steep increase observed in the Cape Grim archive from the late 1980s to the 1990s could not be confirmed with the firn reconstruction. However, the abundances and trends agreed for all compound from the year 2000 on. A recent slow down in growth could be observed for the three shorter-chained PFCs but not for n-C$_7$F$_{16}$. Generally n-C$_4$F$_{10}$ and n-C$_5$F$_{12}$ showed a similar temporal evolution suggesting that these two compounds may have been used in similar applications. The trends of n-C$_6$F$_{14}$ and n-C$_7$F$_{16}$ are less similar to each other although the main reported usage of both compounds is as heat transfer fluids. Measurements of air samples collected in the upper troposphere and stratosphere are consistent with the above findings.

Comparison with a "bottom-up" emission database revealed severe discrepancies to "top-down" emissions derived from our observations in the case of n-C$_4$F$_{10}$ and n-C$_5$F$_{12}$. We find that emissions from these two compounds are underreported by several orders of magnitude in the EDGAR emission database. In the case of n-C$_7$F$_{16}$ the disagreement was less pronounced but still significant. However, it should be noted that uncertainties were only available for our top-down approach here. Bottom-up uncertainties could potentially bridge the gap between emission estimates of n-C$_7$F$_{16}$. For n-C$_6$F$_{14}$ we find reasonable agreement between the two emission data sets and conclude that sources are better understood and quantified for this molecule. We also conclude that
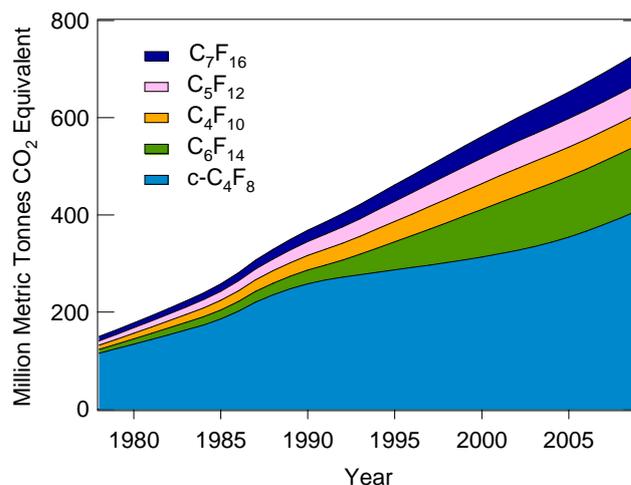
there are significant unknown sources releasing n-C$_4$F$_{10}$ and n-C$_5$F$_{12}$ (and probably n-C$_7$F$_{16}$) into the atmosphere. However, due to the limited number of reporting countries differences between the emission data base and our estimates could well be originating from known applications in countries that have not been reporting these emissions.

When applying the radiative forcings from IPCC, 2007 (C$_4$F$_{10}$: 0.33 Wm^{-2}ppb^{-1}, C$_5$F$_{12}$: 0.41 Wm^{-2}ppb^{-1}, C$_6$F$_{14}$: 0.49 Wm^{-2} ppb^{-1}) and Bravo et al., 2010 (C$_7$F$_{16}$: 0.45 Wm^{-2} ppb^{-1}) to the mixing ratios observed at the end of 2010 at Cape Grim we derive a radiative forcing of 0.285 mWm^{-2} from the sum of the four compounds. This is only 0.017 % of the radiative forcing caused by anthropogenic CO$_2$ in 2005 (IPCC, 2007) and we therefore conclude that their current contribution to global warming is comparably small. Figure 10 shows the cumulative emissions of the four PFCs as CO$_2$ equivalents. As they have atmospheric lifetimes on the order of thousands of years (IPCC, 2007; WMO, 2011) they accumulate almost quantitatively once released into the atmosphere. Emissions of three of the four species reported here have been declining in recent years. The introduction of emission reduction techniques in industrial applications such as the use of alternative chemistries, process optimisation as well as compound destruction, recovery or recycling (Tsai et al., 2002) may well have played a significant role here. However, it would be desirable to minimise their future emissions further as these compounds have already contributed the equivalent of 325 million tonnes of CO$_2$ to global warming by the end of 2009 (Fig. 10). When including emissions of c-C$_4$F$_8$ (updated from Oram et al., 2012)

the cumulative emissions of C4 to C7 PFCs exceeded 750 million tonnes of CO_2 equivalents by this time.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/12/4081/2012/acp-12-4081-2012-supplement.pdf.

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