Emissions halted of the potent greenhouse gas \( \text{SF}_5\text{CF}_3 \)

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Abstract

Long term measurements in background air (Cape Grim, Tasmania) and firn air (NEEM, Greenland) of the “super” greenhouse gas SF$_5$CF$_3$ show that emissions declined after the late 1990s, having grown since the 1950s, and became indistinguishable from zero after 2003. It is concluded that this is due to the cessation of global production of perfluorooctyl sulfonate-based fluorochemicals. An earlier observation of closely correlated atmospheric abundances of SF$_5$CF$_3$ and SF$_6$ are shown here to have likely been purely coincidental, as their respective trends diverged after 2002. Due to its long lifetime (ca. 900 yr), atmospheric concentrations of SF$_5$CF$_3$ have not declined, and it is now well mixed between hemispheres, as is also shown here from interhemispheric aircraft measurements. Total cumulative emissions of SF$_5$CF$_3$ amount to around 5 kT.

1 Introduction

In recent years the atmospheric growth of a number of fully-fluorinated and very long-lived greenhouse gases (“super” greenhouse gases), with lifetimes on the order of a thousand years or more, has been observed; e.g. CF$_4$ and C$_2$F$_6$ (Worton et al., 2007), C$_3$F$_8$ (Mühle et al., 2010), c-C$_4$F$_8$ (Oram et al., 2011), NF$_3$ (Weiss et al., 2008) and SF$_6$ (Levine et al., 2010). These gases have exceptionally high Global Warming Potentials (GWPs), in some cases on the order of several thousand times that of CO$_2$, and thus their unconstrained growth would be of considerable concern for the radiative forcing of climate.

In 2000 we reported our discovery of another, entirely unexpected, perfluorocarbon, namely SF$_5$CF$_3$ (Sturges et al., 2000). This was initially noticed as unidentified mass chromatographic peaks with m/z ratios representative of CF$_3^+$ and SF$_5^+$ ions during measurements of chlorofluorocarbons and SF$_6$ in air samples from the middle stratosphere. The appearance of this substance in air samples from above 32 km altitude

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immediately implied that the “mystery” compound had to be long-lived. Two features marked this compound out as exceptional. Firstly, we determined that as a molecule it had the highest radiative forcing efficiency of any gas yet measured in the atmosphere (0.57 W m\(^{-2}\) ppb\(^{-1}\)). Secondly, it appeared to have grown in the atmosphere, between the mid-20th century and 1999, at almost exactly the same rate as SF\(_6\), to which it is closely chemically related. From this circumstantial evidence we concluded that its origins might be related to those of SF\(_6\), and we conjectured that it might be formed from high energy arc discharge in electrical equipment containing SF\(_6\) as a high voltage dielectric. Indeed there has since been some laboratory evidence for this (Huang et al., 2005; Solovev et al., 2007). Immediately following publication of our article, however, an open letter to the publishing journal from the company 3M stated that “one source of this compound is as a by-product of the manufacture of certain 3M fluorochemicals” (Santoro et al., 2000). It transpired that the relevant process was electrochemical fluorination for the production of perfluorooctanyl sulphonate, (PFOS) and other fluorosurfactants, used in the manufacture of foams and stain-resist coatings. They went on to note that these production operations were to be imminently curtailed in the USA. In a subsequent personal communication, their bottom-up emission estimates were evidently close to the global emission rate that we had deduced from observations.

Our updated atmospheric measurements, presented here, clearly demonstrate that our original supposition that SF\(_5\)CF\(_3\) originates from degradation of SF\(_6\) was incorrect, and that all evidence points to 3M being correct in their assertion and that, as they had predicted, emissions of this potent greenhouse gas have subsequently reduced to the point where they are not distinguishable by observation from zero.
2 Methodology

2.1 Sampling and analysis

The majority of the samples collected at Cape Grim, Tasmania (40.4° S, 144.4° E) since 1994 were pumped directly into 3-dm$^3$ electrochemically passivated (Rasmussen) or Silcosteel-treated (Restek Corp.) stainless steel canisters at a pressure of ca. 2 atmospheres using a metal bellows air pump. Prior to 1994, the samples analysed were sub sampled from the parent Cape Grim air archive contained at high pressure (ca. 30 atmospheres) in large (35 dm$^3$) stainless steel vessels. In all cases the air samples were collected under baseline (clean marine air) conditions. Details of the Cape Grim air archive and sampling techniques have been reported elsewhere (Oram et al., 1995; Fraser et al., 1999). Analyses were carried out using gas chromatography separation followed by detection with an EBE configuration triple-sector mass spectrometer (Waters/Micromass “Autospec”). Two slightly different techniques were employed using different capillary columns in the case of the Cape Grim air samples. In the first instance samples were preconcentrated on a glass bead trap cooled to around −185°C and separated on a Chrompack KCl-passivated alumina PLOT column. In the second case the samples were preconcentrated on a Hayesep D-packed trap cooled to −78°C. The two techniques are described in detail in Oram et al. (2011). Samples from NEEM and CARIBIC (see below) were exclusively analysed using the GasPro column. Analytical uncertainties were assessed from the reproducibility of duplicate samples and frequent calibration standard measurements.

To determine a corresponding time trend of SF$_5$CF$_3$ in the Northern Hemisphere we also made measurements on air pumped from deep snow (firn) in Northern Greenland (the North Greenland Eemian Ice Drilling project, NEEM; http://www.neem.nbi.ku.dk), which contains air dating from the early 20th century (Buizert et al., 2011). The sampling for trace gases at NEEM is described in Buizert et al. (2011) and Laube et al. (2010).
Finally, measurements were also made on 49 air samples collected from a Lufthansa aircraft during four flights at cruising altitudes of 8.6 to 12.2 km between Frankfurt, Germany and Cape Town/Johannesburg, South Africa in the period October 2009 to March 2011 in the framework of the CARIBIC project (Brenninkmeijer et al., 2007; http://www.caribic-atmospheric.com).

2.2 2-D atmospheric modelling

A 2-D global atmospheric chemistry-transport model was used to derive “top-down” emission estimates of SF$_5$CF$_3$ from the measurements made at Cape Grim. The model grid is divided into 24 equal area, longitudinally-averaged bands and has 12 vertical layers each of 2 km depth. The model has been described elsewhere (Hough 1989, 1991) and has been used to study the temporal behaviour and global distribution of other halocarbons (Fraser et al., 1999; Reeves et al., 2005; Laube et al., 2010; Oram et al., 2011). The latitudinal distribution of emissions is based on an even split between the two main production sites of PFOS by 3M, Decatur, Alabama (34° N, 87° W) and Antwerp, Belgium (51° N, 4° E) (Paul et al., 2009). An atmospheric lifetime of 890 years was assumed for SF$_5$CF$_3$ (Montzka et al., 2010; Miller et al., 2002), and the annual emissions in the model were adjusted until the predicted concentrations matched the Cape Grim observations.

2.3 Modelling trace gas transport in firn

The relationship between past atmospheric time trends and concentration profiles in firn can be established using models of trace gas transport in firn, which is dominated by diffusion but is also subject to gravitational fractionation, firn sinking and gas trapping effects. Here we use a direct model of transport in firn as described by Witrant et al. (2011), which includes the main modelling principles proposed by Rommelaere et al. (1997), Fabre et al. (2000) and Martinerie et al. (2009). We use a firn diffusivity for the conditions at NEEM that has been evaluated using nine reference gases: CO$_2$,
CH₄, SF₆, HFC-134a, CH₃CCl₃, ¹⁴CO₂, CFC-11, CFC-12 and CFC-113 as described in greater detail in Buizert et al. (2011). The diffusion coefficient for SF₅CF₃ was taken to be the same as that used in our earlier study (i.e. 0.0562 cm² s⁻¹, or 0.467 relative to that of CO₂; Sturges et al., 2000).

3 Results and discussion

The Cape Grim measurements are compiled in Fig. 1 as red diamonds for the measurements made with the GasPro capillary column, and green dashes for those made with the Al-PLOT capillary column. There is excellent agreement between the two sets of analyses for the overlapping time periods. The Al-PLOT measurements, however, had somewhat lower precision and were more scattered. The reason for this is not entirely clear (it might relate to slightly higher column bleed) as other gases showed generally excellent precision by the same method (e.g., Worton et al., 2007). Also shown, as blue circles, are the measurements from the original SF₅CF₃ paper. These were all from measurements in Antarctic firn air (Dome Concordia) and the dates have been estimated from co-measurements of SF₆ as described in Sturges et al. (2000). The tabulated dates so determined can be found at the Carbon Dioxide Information Analysis Center (http://cdiac.ornl.gov/trends/otheratg/sturges/sturges.html). The Dome C measurements usefully extend the southern hemispheric trend to dates before that of first Cape Grim measurements. The final set of measurements shown in Fig. 1 is the means of the measurements from the flights of the CARIBIC aircraft in 2009, 2010 and 2011 in the upper troposphere and lower stratosphere. These agree very well with the last few years of SF₅CF₅ measurements at Cape Grim, which is discussed further below.

Due to the greater scatter of the Cape Grim Al-PLOT measurements, we have based our subsequent model and curve fitting on the Cape Grim GasPro measurements, but we have also included the Dome C measurements prior to 1978 to define the earlier part of the trend. A five-parameter sigmoid expression (SPSS, now Systat Software, SigmaPlot Version 7) has been used to fit a smoothed line to the points (dashed blue-
green line), as this allows an envelope of uncertainty to be plotted based on the ±1
sigma deviation of the fit (dashed black lines). The 2-D atmospheric model output for
the surface grid box for the latitude of Cape Grim is shown as a solid red line. This is
barely distinguishable from the sigmoidal line fit, and falls entirely within the deviation
of the latter, as can be better seen in the expanded panel (inset). We therefore judge
that the model fit represents well the observed trend.

The final curve plotted in Fig. 1, shown as a blue broken line, is a calculation of the
SF$_5$CF$_3$ abundance expected had it exhibited the same relative molar abundance to
SF$_6$ as was assumed in the modelling study from our original paper, i.e. a ratio to SF$_6$
of 3.05 × 10$^{-2}$. After 2002 it is clear that the apparent relationship between SF$_5$CF$_3$ and
SF$_6$ began to diverge, with the latter continuing to grow whilst the SF$_5$CF$_3$ abundance
began to stabilise. It can, therefore, be concluded that the emission of SF$_5$CF$_3$ is not
linked to that of SF$_6$, contrary to our original hypothesis.

The measurements in Fig. 1 demonstrate the absence of significant emissions of
SF$_5$CF$_3$ prior to the late 1960s, which is consistent with large-scale manufacture of
PFOS having begun after 3M acquiring the patent for electrochemical fluorination in
the 1950s. The first evidence for an unambiguous decrease in the atmospheric growth
rate appears to have been around 2000, since which time the growth rate has declined
rapidly. For the model to agree with the sigmoidal line fit, it was necessary to continue
a small emission to the atmosphere after 2003 (see below). However, a model run (not
shown) in which emissions were allowed to continue until 2003, and were then reduced
to zero thereafter, resulted in a small decline in SF$_5$CF$_3$ (less than 1 % or 0.001 ppt)
between 2003 and 2011, but which still fell within the uncertainty of the measurements.
Equally, a longer atmospheric lifetime would imply emissions closer to zero, as noted
in a sensitivity test with a lifetime of 3000 yr (not shown).

The observed trend is broadly consistent with Rosiek et al. (2007) who reported
a continuing upward trend between 2001 and 2003 in Krakow, Poland, and an appar-
ent subsequent slow-down in the growth rate of SF$_5$CF$_3$ reported by Busenberg and
Plummer (2008) from various sites in North America.
The annual emissions used in the atmospheric model to reproduce the observed atmospheric abundance of SF$_5$CF$_3$ are shown in Fig. 2. Emissions rose year-on-year from the 1960s to the 1990s, peaking around 1996 at around 300 t before progressively declining. The decline was very rapid from about 2000 to 2003. As discussed above, we cannot confidently distinguish the emissions shown after 2003 (around 10 t yr$^{-1}$) from zero.

The same model run can also be used to produce a temporal trend for the latitude and elevation relevant to the Greenland firn air sampling site. This trend can then be used as input to the firn diffusion model to derive an expected depth profile for SF$_5$CF$_3$. This is shown in Fig. 3 (line) along with the actual measurements made in the firn air (symbols). There is very good agreement suggesting excellent compatibility between the two sets of measurements and further validation of the modelled atmospheric distribution of SF$_5$CF$_3$.

The model computed no significant latitudinal gradient, and also no altitudinal gradient up to the tropopause, for the latter years (2005 onwards). This is confirmed by the agreement between the CARIBIC measurements in 2009, 2010 and 2011 in the upper troposphere/lower stratosphere, and the ground level measurements from NEEM (albeit made at about 3 km) and from Cape Grim (Fig. 1). Figure 4 further illustrates that, by the date of the aircraft flights, there was no evidence of a latitudinal gradient in SF$_5$CF$_3$, which also confirms the absence of further significant emissions to the atmosphere, such that the mixing ratio of this gas had equilibrated throughout the global atmosphere.

3M stated that a phase-out of PFOS manufacture was decided upon in 2000 (statement on “3M’s Phase Out and New Technologies” at http://solutions.3m.com/wps/portal/3M/en_US/PFOS/PFOA/Information/phase-out-technologies/), but also that overall greenhouse gas emissions (not just SF$_5$CF$_3$) had been reduced 40% since 1995 (Santoro, 2000). The PFOS phase-out was supposedly completed in 2002 (see “statement” above on 3M’s web site). Our results confirm that there was indeed a rapid decline in emissions between 2000 and 2003, although the uncertainties in
our observations preclude us from determining whether emissions actually ceased in 2003. Nevertheless, these findings strongly suggest that SF$_5$CF$_3$ emissions are indeed uniquely associated with such fluorochemical production. 3M state that associated fluorochemical production continued via a subsidiary (Dyneon), albeit using perfluorooctanoic acid (PFOA) not PFOS, but this too ceased in 2008 (see 3M “statement”). A number of companies worldwide continue to manufacture related perfluorocarboxylates (Rennrner, 2006) but, it appears from our observations, without incurring substantial emissions of SF$_5$CF$_3$. 3M themselves have subsequently switched to processes that produce perfluorobutane sulfonate (PFBS) instead of the more toxic PFOS (3M “statement” and Renner, 2006).

4 Conclusions

The combined dataset from the Cape Grim atmospheric air archive, northern and southern hemispheric firn air, and interhemispheric aircraft flights results in a consistent atmospheric trend for SF$_5$CF$_3$ from the mid-20th century to 2011. Although the maximum atmospheric abundance of this molecule has never exceeded more than a small amount (0.15 ppt), and thus currently contributes only minutely to climate forcing (Sturges et al., 2000), it (along with the other fully-fluorinated species referred to in the Introduction) represents an essentially irreversible change to the composition of the Earth’s atmosphere and to the radiative forcing of the climate. The present cessation (or near-cessation), and presumed future avoidance of further emissions of this gas, is therefore to be welcomed.

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Fig. 1. The atmospheric record of SF$_5$CF$_3$ from measurements made in air collected at Cape Grim, Tasmania, in firn air collected at Dome Concordia, Antarctica, and in air collected between 8.6 and 12.2 km and 47° N–28° S from the CARIBIC aircraft. The dashed blue-green line is a least mean squares optimisation fit to a subset of the Cape Grim (see text) and Dome Concordia measurements (pre-1978) with the uncertainty of the fit shown as black dashed lines. The red line (almost indistinguishable from the blue-green line) is the output mixing ratio from the atmospheric model run for the location of Cape Grim using the emissions shown in Fig. 2. The blue broken line shows the “predicted” SF$_5$CF$_3$ assuming a constant ratio to SF$_6$ (see text). The inset figure is an expansion of the main graph between the dates 2000–2011.
Fig. 2. The model-derived annual and cumulative emissions of SF$_5$CF$_3$ used to produce the atmospheric model fit scenario presented in Fig. 1 (the red line in Fig. 1).
Fig. 3. The observed amounts (symbols) of SF$_5$CF$_3$ in samples collected at different depths of firn at the NEEM drilling site, Greenland. The purple line is the result of taking the long-term trend of the gas in the atmospheric model domain box appropriate for NEEM, based on the best fit to Cape Grim (red line in Fig. 1), and used as input to the firn diffusion model.
Fig. 4. Measurements of SF$_5$CF$_3$ from whole air samples collected from four interhemispheric CARIBIC flights flying at 8.6–12.2 km, as a function of latitude.