Atmospheric histories and growth trends of C₄F₁₀, C₅F₁₂, C₆F₁₄, C₇F₁₆ and C₈F₁₈

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Abstract

The first atmospheric observations and trends are presented for the high molecular weight perfluorocarbons (PFCs): decafluorobutane (C$_4$F$_{10}$), dodecafluoropentane (C$_5$F$_{12}$), tetradecafluorohexane (C$_6$F$_{14}$), hexadecafluoroheptane (C$_7$F$_{16}$) and octadecafluoroctane (C$_8$F$_{18}$). Their atmospheric histories are based on measurements of 38 Northern Hemisphere and 46 Southern Hemisphere archived air samples collected between 1973 to 2011 using the Advanced Global Atmospheric Gases Experiment (AGAGE) “Medusa” preconcentration gas chromatography-mass spectrometry systems. A new calibration scale was prepared for each PFC, with estimated accuracies of 6.8% for C$_4$F$_{10}$, 7.8% for C$_5$F$_{12}$, 4.0% for C$_6$F$_{14}$, 6.6% for C$_7$F$_{16}$ and 7.9% for C$_8$F$_{18}$. Based on our observations the 2011 globally averaged dry air mole fractions of these heavy PFCs are: 0.18 parts-per-trillion (ppt, i.e., parts per 10$^{12}$) for C$_4$F$_{10}$, 0.12 ppt for C$_5$F$_{12}$, 0.28 ppt for C$_6$F$_{14}$, 0.12 ppt for C$_7$F$_{16}$ and 0.09 ppt for C$_8$F$_{18}$. These atmospheric mole fractions combine to contribute to a global average radiative forcing of 0.35 mW m$^{-2}$, which is 3.6% of the total PFC radiative forcing. The globally averaged mean atmospheric growth rates of these PFCs during 1973–2011 are 4.58 parts per quadrillion (ppq, i.e., parts per 10$^{15}$) per year (yr) for C$_4$F$_{10}$, 3.29 ppq yr$^{-1}$ for C$_5$F$_{12}$, 7.50 ppq yr$^{-1}$ for C$_6$F$_{14}$, 3.19 ppq yr$^{-1}$ for C$_7$F$_{16}$ and 2.51 ppq yr$^{-1}$ for C$_8$F$_{18}$. The growth rates of the heavy perfluorocarbons were largest in the early 1990s for C$_4$F$_{10}$ and C$_5$F$_{12}$ and in the mid-to-late 1990s for C$_6$F$_{14}$, C$_7$F$_{16}$ and C$_8$F$_{18}$. The more recent slow down in the growth rates of the high molecular weight PFCs suggests that emissions are declining as compared to the 1980s and 1990s. Nevertheless continued monitoring of these potent, extremely long-lived greenhouse gases is necessary to verify that global PFC emissions continue to decline.
1 Introduction

Perfluorocarbons (PFCs) are powerful greenhouse gases regulated under the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC). Due to their long lifetimes and strong absorption in the infrared, PFCs are considered to have a permanent effect on the Earth’s radiative budget and have global warming potentials (GWPs) 3 to 4 orders of magnitude higher than that of carbon dioxide (CO₂), see Table 1, (Forster et al., 2007). Observations and optimized emission estimates are available for the lower molecular weight PFCs: carbon tetrafluoride (CF₄), hexafluoroethane (C₂F₆), octafluoropropane (C₃F₈) and octafluorocyclobutane (c-C₄F₈) (Mühle et al., 2010; Oram et al., 2012; Saito et al., 2010). CF₄ is the most abundant PFC and has a significant natural abundance (Deeds et al., 2008; Harnisch et al., 1996a,b; Mühle et al., 2010). The predominant anthropogenic emissions of the lower molecular weight PFCs are from the production of aluminum, usage in the semiconductor industry and as refrigerants (Mühle et al., 2010; Oram et al., 2012). Both the aluminum and semiconductor industries have made efforts to reduce emissions of the lower molecular weight PFCs to the atmosphere, although global bottom-up inventories do not agree with atmospheric measurement based top-down emission estimates (Mühle et al., 2010; International Aluminium Institute, 2011; Semiconductor Industry Association, 2001; World Semiconductor Council, 2005).

Currently, there are no published observations or top-down emission estimates based on atmospheric measurements for the higher molecular weight PFCs: decafluorobutane (C₄F₁₀), dodecafluoropentane (C₅F₁₂), tetradecafluorohexane (C₆F₁₄), hexadecafluoroheptane (C₇F₁₆) and octadecafluorooctane (C₈F₁₈). These PFCs have emission sources similar to other halocarbons, e.g. their usage as refrigerants, solvents, fire suppressants and foam blowing agents; they were initially suggested as replacements for ozone depleting substances (ODS) that are regulated under the Montreal Protocol (UNEP Technology and Economic Assessment Panel, 1999; Tsai, 2009). Moreover, C₅F₁₂-C₈F₁₈ (liquids at room temperature), have a first-in-kind emission
source from their use as heat transfer fluids in the semiconductor industry (Tsai, 2009; Tuma and Tousignant, 2001). In this study, the first atmospheric observations of $C_4F_{10}$, $C_5F_{12}$, $C_6F_{14}$, $C_7F_{16}$ and $C_8F_{18}$ are presented based on measurements of Northern Hemisphere (NH) and Southern Hemisphere (SH) archived air samples. These samples cover a 39-year period, from 1973 to 2011, and include 38 NH and 46 SH separate samples. Additionally, long-term growth trends are presented based on the atmospheric histories for the high molecular weight PFCs.

2 Experimental methods

2.1 Instrumentation

The cryogenic preconcentration gas chromatography-mass spectrometry (GC-MS: Agilent 6890-5973/5975) “Medusa” systems (Miller et al., 2008) were used to measure the heavy PFC mole fractions in archived air samples at the Scripps Institution of Oceanography (SIO), University of California, San Diego (San Diego, CA) and at the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Division of Marine and Atmospheric Research (CMAR, Aspendale, Australia). These instruments are part of the Advanced Global Atmospheric Gases Experiment (AGAGE) network. For each measurement, the condensables in a 2-l air sample are preconcentrated onto a micro-trap and then cryofocused onto a second micro-trap (both micro-traps are initially held at $-160^\circ$C and subsequently heated for desorption) before injection onto a capillary column. Currently, the Medusa systems in AGAGE use a CP-PoraBOND Q fused silica PLOT column (25 m, 0.32 mm ID, 5 µm, Agilent Technologies) as the main column for separation of all analytes (except $CF_4$) (see Miller et al. (2008) for details). However for the measurements at CSIRO, the Medusa was fitted with a GS-GasPro column (60 m, 0.32 mm ID, Agilent Technologies) as the main column, which had improved separation for these analytes. To maximize the measurements precisions, the quadrupole MS was operated in selective ion mode (SIM). Additionally, only a select number of
species were measured in this experiment to further improve sample precisions, as compared to the 50+ species typically measured as part of the AGAGE network. Each sample measurement was bracketed by a reference gas analysis, allowing for correction of short-term instrumental drift (Prinn et al., 2000). A small blank was detected for C$_6$F$_{14}$, C$_7$F$_{16}$ and C$_8$F$_{18}$, most likely due to the Nafion dryers used in the Medusa, and the observations were corrected accordingly. The detection limits for each species on both instruments were estimated as three times the baseline noise of the target ion immediately preceding and following the elution of the species and are presented in Table 2. The differences in the detection limits between the two instruments are due to the improved separation on the GS-GasPro column used on the CSIRO Medusa and the newer model of MS (5975) used at SIO.

Two experiments were done to assess whether the instrument responses of the Medusa systems were linear over the required range of mixing ratios for each species. In general, the instrument response, $R$, is related to the sample mole fractions, $\chi$, by $R \propto \chi^{(1-\epsilon)}$, where $\epsilon$ is the nonlinearity parameter (Prinn et al., 2000). A dry-air sample from a 2010 Cape Grim Air Archive (CGAA) tank was decanted into a 35-l stainless steel tank (Essex Cryogenics), and spiked with a small volume of high-purity methane (CH$_4$) to increase the CH$_4$ mole fractions from ambient to ca. 8 parts per million. From this spiked air sample, six subsamples were prepared in 6-l stainless steel SilcoCan flasks (Restek Inc.) using a vacuum manifold. Each subsample was then diluted by adding “zero-air” (Scott Marrin, that was further purified using a trap of glass beads, activated charcoal, Molecular Sieve 13X and Carboxen 1000 in a dry ice/ethanol bath at $-97^\circ$C). The amount of zero-air added was varied to give a range of dilution factors (nominally from 6.25% to 75%). The actual dilution factors for each subsample were determined by precisely measuring the CH$_4$ mole fractions (including that of the spiked parent sample) on a gas chromatography-flame ionization detector (GC-FID) system with a known linear response (Francey et al., 2003). These subsamples were subsequently measured on the Medusa systems to determine the linearity of the Medusa measurements for each species.
The second experiment to characterize the instrument response involved sampling different volumes from a single air sample (Miller et al., 2008). The range of relative volumes sampled was from 6% to 200% of the standard 2-l sample. The volume method has the advantage of characterizing instrument responses at mole fractions above present day background levels, which could not be easily achieved through the dilution subsamples unless more concentrated samples were prepared. However as the atmospheric samples measured in the air archives were all below current atmospheric background mole fractions, the volume method served only to complement the dilution method’s instrument response experiment. Generally, the systems exhibited a linear response over much of the required range of mole fractions, with departures from linearity at mole fractions corresponding to those of the oldest archive samples, which have the lowest mole fractions. Based on these dilution experiment measurements, a nonlinearity parameter, $\epsilon$, was estimated for each PFC on each instrument and was used to correct the observations.

2.2 Calibration

Primary standards were prepared at SIO to identify and quantify the heavy PFCs on the Medusa. The primary standards were prepared following the bootstrap method by step-wise dilution, with dichlorodifluoromethane (CCl$_2$F$_2$, CFC-12) used as the bootstrap gas (Prinn et al., 2000). The high-purity compounds were purchased from Synquest Laboratories with purities of: C$_4$F$_{10}$ (98 % min.), C$_5$F$_{12}$ (99 % min.), C$_6$F$_{14}$ (98.5 % min.), C$_7$F$_{16}$ (98 % min.) and C$_8$F$_{18}$ (99 % min.); the nitrous oxide (N$_2$O) was purchased from Scott Specialty Gases and had a purity of 99.9997 %, and CFC-12 had a purity of 99.99 %. Each high-purity compound was vacuum distilled for further purification by repeated cycles of freezing with liquid nitrogen, vacuum removal of noncondensable contaminants and then thawing.

First a gravimetric PFC/CFC-12/N$_2$O mixture was prepared with a molar ratio of PFC to CFC-12 of $1.85 - 3.7 \times 10^{-3}$, with CFC-12 being used as the bootstrap gas and N$_2$O as the balance gas. Typically N$_2$O is used as the bootstrap gas; however
these standards were prepared as standard additions and the expected final N₂O mole fractions would have been beyond the range of the currently available SIO calibration scale. Therefore, CFC-12 was used as the bootstrap gas, as the resulting final mole fractions of CFC-12 have been shown to be within the linear range on the Medusa.

A primary standard was prepared by spiking a real air sample filled at La Jolla, CA (32.87° N, 117.25° W) with the PFC/CFC-12/N₂O mixture. The real air sample was measured on the Medusa to measure it’s initial CFC-12 mole fractions and instrument response for each PFC. The additional mole fractions added to the real air sample from the PFC/CFC-12/N₂O spike were ca. 2 parts per trillion (ppt) of C₆F₁₄, 1 ppt of the other PFCs and 540 ppt of CFC-12. The dilution factor of the PFC/CFC-12/N₂O mixture added to the real air sample was determined by measuring the final CFC-12 mole fractions on the Medusa. The final atmospheric mole fractions in the primary standard were estimated as described by Ellison and Thompson (2008).

The primary standard was measured on the Medusa to determine the retention times and mass spectra of the heavy PFCs as well as to quantify the atmospheric observations. Table 2 shows the target and qualifier mass-to-charge ratios used on the SIO and CSIRO Medusa systems; the target mass-to-charge ratio is used for identification and quantitation, while the qualifiers are only used for ensuring the proper identification of the species. Four primary standards were prepared and the calibration scales have estimated accuracies of 6.8 % for C₄F₁₀, 7.8 % for C₅F₁₂, 4.0 % for C₆F₁₄, 6.6 % for C₇F₁₆ and 7.9 % for C₈F₁₈.

3 Archived air samples

The atmospheric histories of these heavy PFCs are based on measurements made at SIO and CSIRO of NH and SH archived air samples, which cover a 39-year period. In total, 38 NH separate samples (35 measured at SIO and 3 measured at CSIRO) with fill dates from 1973 to 2011 were measured. These tanks were filled either at Cape Meares, Oregon (45.50° N, 123.95° W), La Jolla, California (32.87° N, 117.25° W)
or Trinidad Head, California (41.05° N, 124.05° W) during baseline conditions and are from the laboratories of the late C.D. Keeling; R.F. Keeling; and R.F. Weiss at SIO. The fill techniques, tank materials, tank sizes and fill purposes of the tanks varied. Two tanks were rejected as they were clearly identified as outliers with atmospheric mole fractions significantly higher than present day values. From 2003, a collection of tanks containing NH air have been maintained at R.F. Weiss’s laboratory at SIO as an air archive. These tanks were filled at Trinidad Head, California using a modified oil-free compressor (Rix Industries) in 35-l internally electropolished stainless steel cylinders (Essex Cryogenics). Recent filled archive tanks agree with in situ measurements made by the Medusa system at the time of the tank filling for the high molecular weight PFCs studied here, confirming that the modified Rix compressor does not contribute to the integrity of these samples for the high molecular weight PFCs.

Forty-six separate SH samples filled between 1978 and 2010 were also measured (6 at SIO and 40 at CSIRO). All but three of these tanks, which were from the M.A. Whalen laboratory at SIO, are part of the CGAA collection (Krummel et al., 2007; Langenfelds et al., 1996). The CGAA samples analyzed as part of this study consist of whole air samples cryogenically filled in 35-l internally electropolished stainless steel cylinders at the Cape Grim Baseline Air Pollution Station in Tasmania, Australia (40.68° S, 144.69° E), except for three which were cryogenically collected in 48-l aluminum cylinders; these latter three samples were rejected for their C8F18 values as they were significantly higher than present-day background mole fractions. Four archive samples, all collected in 2001, had significantly higher than current baseline mole fractions for C7F16 and these values were consequently flagged as contaminated; these included the three tanks from the M.A. Whalen laboratory and one CGAA tank.

Seven subsamples of the CGAA, covering the time period of 1986 to 2008, were decanted into 4.5-l internally electropolished stainless steel cylinders (Essex Cryogenics) and subsequently measured on the SIO Medusa system; the parent samples were measured at CSIRO. This was to check whether the two instruments and the calibration propagations produced measurements that agreed within known uncertainties.
Generally, the measurements on the two systems agreed well within the measurement uncertainty, with a maximum difference of 0.0088 ppt for C₈F₁₈. For both sets of archived samples, at least 3 replicate measurements were made of each sample; for younger samples, 5 to 6 replicate measurements were made since more air was available. The measurement errors on the samples are estimated as the 1-σ standard deviations of the repeat measurements.

4 Results and discussion

The atmospheric histories from 1973 to 2011 for the high molecular weight PFCs studied here are shown in Fig. 1. C₄F₁₀ and C₅F₁₂ are present in the earliest archived samples at 0.015 ppt and 0.011 ppt, respectively. C₄F₁₀ and C₅F₁₂ exhibit quasi-exponential growth in the 1980s and early 1990s and then grow linearly to present day globally averaged background atmospheric mole fractions of 0.18 ppt and 0.12 ppt, respectively. The slow-down in growth rates in the mid-1990s suggest that emissions were decreasing, as is supported by the decreases in the inter-hemispheric gradients, for C₄F₁₀ and C₅F₁₂. Emissions of these high molecular weight PFCs are of anthropogenic origin and primarily released in the Northern Hemisphere. Therefore as is expected, we see higher atmospheric mole fractions in the Northern Hemisphere than in the Southern Hemisphere due to the 1 to 2 year mixing time between the two hemispheres. Additionally, higher variability in the NH samples can be seen, as compared to the SH samples. This is attributed to sampling of less well mixed air due to emissions originating primarily in the NH, although efforts are made to fill the archive tanks during baseline conditions.

C₆F₁₄ and C₇F₁₆ are not detectable in the archived samples until 1985 and grow quasi-exponentially until 1999. C₈F₁₈ follows a similar trend to those of C₆F₁₄ and C₇F₁₆, although it is not detectable until the mid-1990s, which could be due to its higher detection limit than for C₆F₁₄ and C₇F₁₆. After 1996 the growth rates of C₆F₁₄, C₇F₁₆ and C₈F₁₈ slow, suggesting a decline in global emissions. The most abundant of these heavy PFCs is C₆F₁₄ at a globally averaged background tropospheric mole...
fraction of 0.28 ppt in 2011. The globally averaged atmospheric mole fraction in 2011 is 0.12 ppt for C\textsubscript{7}F\textsubscript{16}, and C\textsubscript{8}F\textsubscript{18} is the least abundant of all of these PFCs at 0.09 ppt. In general, the NH archived air samples have higher atmospheric mole fractions than the SH samples with similar fill dates, suggesting that the emissions are primarily in the NH, as was seen for C\textsubscript{4}F\textsubscript{10} and C\textsubscript{5}F\textsubscript{12}. There is one anomalous NH tank with a fill date in 1986 for C\textsubscript{6}F\textsubscript{14}, C\textsubscript{7}F\textsubscript{16} and C\textsubscript{8}F\textsubscript{18}, which has lower atmospheric mole fractions than the SH tanks with similar fill dates. However, this 1986 NH air sample is below the detection limit of the SIO instrument; additionally, the tank was not filled for the purpose of an air archive and has been to shown to have non-background mole fractions for C\textsubscript{2}F\textsubscript{6}, C\textsubscript{3}F\textsubscript{8} and sulfur hexafluoride (SF\textsubscript{6}).

Due to the sparseness of the available data set, the presented growth rates are based on cubic smoothed spline fits to the observations. The observations were weighted by their measurement uncertainty and a 50% attenuation period of 5 years was used, which is slightly larger than the mean data-spacing, in estimating the smoothing splines (Enting et al., 2006). The smoothed spline fits are shown along with the observations in Fig. 1. Table 3 shows the 2011 globally averaged background atmospheric mole fractions, and the average global mole fractions and growth rates from 1973 to 2011, which are based on the cubic smoothed spline fits to the observations. Figure 2 shows the annual growth rates estimated from the cubic smoothed spline fit to each PFC observations in each hemisphere. The fastest growth rates were in the late 1980s and early 1990s for C\textsubscript{4}F\textsubscript{10} and C\textsubscript{5}F\textsubscript{12}, while the growth rates for C\textsubscript{6}F\textsubscript{14}, C\textsubscript{7}F\textsubscript{16} and C\textsubscript{8}F\textsubscript{18} peaked later in the 1990s. Additionally, we see the SH growth rates generally lagging the NH growth rates, also confirming that the emissions are primarily in the NH. The growth rates of these heavy PFCs have been decreasing for the past 10 to 15 years to the 2011 globally averaged growth rates of: 2.31 ppq yr\textsuperscript{-1} for C\textsubscript{4}F\textsubscript{10}, 1.38 ppq yr\textsuperscript{-1} for C\textsubscript{5}F\textsubscript{12}, 5.58 ppq yr\textsuperscript{-1} for C\textsubscript{6}F\textsubscript{14}, 3.68 ppq yr\textsuperscript{-1} for C\textsubscript{7}F\textsubscript{16} and 0.99 ppq yr\textsuperscript{-1} for C\textsubscript{8}F\textsubscript{18}. This decrease in growth rates, suggest a decrease in emission rates; although, C\textsubscript{7}F\textsubscript{16} appears to have a more constant growth rate at the end, suggesting only a slight decline in emissions.
Based on the globally averaged 2011 atmospheric mole fractions (Table 3), the global radiative forcing of each PFC can be estimated using the radiative efficiencies presented in Table 1. For $C_4F_{10}$, $C_5F_{12}$ and $C_6F_{14}$ we use the radiative efficiencies given by Forster et al. (2007), and for $C_7F_{16}$ and $C_8F_{18}$, we use the radiative efficiencies given by Ivy et al. (2012). $C_6F_{14}$ contributes the most of these high molecular weight PFCs to the global radiative forcing in 2011, and is similar to that of $C_3F_8$. The other PFCs in this study contribute approximately equally to global radiative forcing; and in total the high molecular weight PFCs 2011 atmospheric mole fractions contribute to a globally averaged radiative forcing of 0.35 mW m$^{-2}$.

5 Conclusions and future implications

Atmospheric histories and long-term growth trends have been presented for the first time for the high molecular weight PFCs: $C_4F_{10}$, $C_5F_{12}$, $C_6F_{14}$, $C_7F_{16}$ and $C_8F_{18}$. The histories and trends are based on new measurements of a collection of NH archived air samples and a subset of the CGAA. The measurements were made with the Medusa systems and are calibrated against new primary standards for these PFCs. The contribution of all of the heavy PFCs studied here to global radiative forcing is 0.35 mW m$^{-2}$. While this is relatively small compared to the total radiative forcing of 2434 mW m$^{-2}$ in 2008 for all species regulated under the Kyoto Protocol, the heavy PFC atmospheric mole fractions in 2011 contribute up to 3.6% of the total PFC radiative forcing (Montzka and Reimann, 2011; Mühle et al., 2010; Oram et al., 2012).

The heavy PFCs in this study exhibited the largest growth in the 1980s and 1990s and have since slowed, suggesting that recent emissions may be decreasing as alternative compounds, with most likely lower GWPs, are used. Based on previous studies, atmospheric observations are crucial in providing measurement-based emission estimates to verify bottom-up inventories, which often show large discrepancies (Mühle et al., 2010; Oram et al., 2012). Additionally, future observations of these high molecular weight PFCs will be important in confirming that the aluminum and semiconductor...
industries, which primarily focus on the low molecular weight PFCs, are indeed reducing global PFC emissions. Although PFCs contribute a relatively small amount to global radiative forcing, as compared to other greenhouse gases, due to their long lifetimes PFCs are considered to have a permanent effect on the Earth’s radiative budget.

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References


Tsai, W.: Environmental hazards and health risk of common liquid perfluoro-n-alkanes, potent


Table 1. Lifetimes, Radiative Efficiencies and Global Warming Potentials of Perfluorocarbons.

<table>
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<tr>
<th>Species</th>
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\textsuperscript{a} Forster et al. (2007)
\textsuperscript{b} Bravo et al. (2010)
\textsuperscript{c} Ivy et al. (2012)
\textsuperscript{d} Shine et al. (2005)
Table 2. Target and Qualifier Mass-to-Charge Ratios, Standard Precisions and Detection Limits for C_{4}F_{10}, C_{5}F_{12}, C_{6}F_{14}, C_{7}F_{16} and C_{8}F_{18}.

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<td>119</td>
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<td>219</td>
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<td>PoraBOND</td>
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<td>PoraBOND</td>
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<td>119</td>
<td>69</td>
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<td>0.0153</td>
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</table>
Table 3. Global Mean (from 1973 to 2011) Mole Fractions and Growth Rates, 2011 Mole Fractions and Radiative Forcing of $C_4F_{10}$, $C_5F_{12}$, $C_6F_{14}$, $C_7F_{16}$ and $C_8F_{18}$.

<table>
<thead>
<tr>
<th>Species</th>
<th>Mean Mole Fractions [ppt]</th>
<th>Mean Growth Rate [ppq yr$^{-1}$]</th>
<th>2011 Mole Fractions [ppt]</th>
<th>2011 Radiative Forcing [mW m$^{-2}$]</th>
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</thead>
<tbody>
<tr>
<td>$C_4F_{10}$</td>
<td>0.101</td>
<td>4.58</td>
<td>0.18</td>
<td>0.059</td>
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<td>$C_5F_{12}$</td>
<td>0.072</td>
<td>3.29</td>
<td>0.12</td>
<td>0.049</td>
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<tr>
<td>$C_6F_{14}$</td>
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<td>7.50</td>
<td>0.28</td>
<td>0.137</td>
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<tr>
<td>$C_7F_{16}$</td>
<td>0.053</td>
<td>3.19</td>
<td>0.12</td>
<td>0.058</td>
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<tr>
<td>$C_8F_{18}$</td>
<td>0.043</td>
<td>2.51</td>
<td>0.09</td>
<td>0.051</td>
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</table>
Fig. 1. Atmospheric mole fractions of C$_4$F$_{10}$, C$_5$F$_{12}$, C$_6$F$_{14}$, C$_7$F$_{16}$ and C$_8$F$_{18}$ based on Northern Hemisphere (green circles) and Southern Hemisphere (pink circles) archived air sample measurements. The vertical bars on the observations denote the 1-σ standard deviations of the sample measurements (often the measurement uncertainty is too small to be seen on the figure). The green and pink lines are the best fits to the NH and SH observations, respectively. The shading shows the detection limits for the two Medusa systems, with light grey for the SIO Medusa and dark grey for the CSIRO Medusa system.
**Fig. 2.** Annual Northern Hemisphere and Southern Hemisphere atmospheric growth rates based on cubic smoothed splines to the observations in parts per quadrillion [ppq] per year, see Sect. 4 for details on fits.