Perfluorocarbons in the global atmosphere: tetrafluoromethane, hexafluoroethane, and octafluoropropane

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Abstract. We present atmospheric baseline growth rates from the 1970s to the present for the long-lived, strongly infrared-absorbing perfluorocarbons (PFCs) tetrafluoromethane (CF\textsubscript{4}), hexafluoroethane (C\textsubscript{2}F\textsubscript{6}), and octafluoropropane (C\textsubscript{3}F\textsubscript{8}) in both hemispheres, measured with improved accuracies (∼1–2%) and precisions (<0.3%, or <0.2 ppt (parts per trillion dry air mole fraction), for CF\textsubscript{4}; <1.5%, or <0.06 ppt, for C\textsubscript{2}F\textsubscript{6}; <4.5%, or <0.02 ppt, for C\textsubscript{3}F\textsubscript{8}) within the Advanced Global Atmospheric Gases Experiment (AGAGE). Pre-industrial background values of 34.7±0.2 ppt CF\textsubscript{4} and 0.1±0.02 ppt C\textsubscript{2}F\textsubscript{6} were measured in air extracted from Greenland ice and Antarctic firn. Anthropogenic sources are thought to be primary aluminum production (CF\textsubscript{4}, C\textsubscript{2}F\textsubscript{6}, C\textsubscript{3}F\textsubscript{8}), semiconductor production (C\textsubscript{2}F\textsubscript{6}, CF\textsubscript{4}, C\textsubscript{3}F\textsubscript{8}) and refrigeration use (C\textsubscript{3}F\textsubscript{8}). Global emissions calculated with the AGAGE 2-D 12-box model are significantly higher than most previous emission estimates. The sum of CF\textsubscript{4} and C\textsubscript{2}F\textsubscript{6} emissions estimated from aluminum production and non-metal production are lower than observed global top-down emissions, with gaps of ∼6 Gg/yr CF\textsubscript{4} in recent years. The significant discrepancies between previous CF\textsubscript{4}, C\textsubscript{2}F\textsubscript{6}, and C\textsubscript{3}F\textsubscript{8} emission estimates and observed global top-down emissions estimated from AGAGE measurements emphasize the need for more accurate, transparent, and complete emission reporting, and for verification with atmospheric measurements to assess the emission sources of these long-lived and potent greenhouse gases, which alter the radiative budget of the atmosphere, essentially permanently, once emitted.

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Table 1. Lifetimes and global warming potentials of CF$_4$, C$_2$F$_6$, and C$_3$F$_8$.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>Lifetime</th>
<th>Global Warming Potential (GWP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>years</td>
<td>(100-yr horizon)</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>PFC-14</td>
<td>50,000</td>
<td>6500</td>
</tr>
<tr>
<td>C$_2$F$_6$</td>
<td>PFC-116</td>
<td>10,000</td>
<td>9200</td>
</tr>
<tr>
<td>C$_3$F$_8$</td>
<td>PFC-218</td>
<td>2600</td>
<td>7000</td>
</tr>
</tbody>
</table>

a IPCC Second Assessment Report;  
b IPCC Fourth Assessment Report.

1 Introduction

The perfluorocarbons (PFCs) tetrafluoromethane (CF$_4$, PFC-14), hexafluoroethane (C$_2$F$_6$, PFC-116), and octafluoropropane (C$_3$F$_8$, PFC-218) are among the longest-lived and most potent greenhouse gases (GHGs) regulated under the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC). CF$_4$ is the most abundant PFC with an atmospheric lifetime of at least 50,000 years and a global warming potential (GWP$_{100}$) of at least 7390 (100-yr horizon) (Cicerone, 1979; Ravishankara et al., 1993; Morris et al., 1995; Jain et al., 2000; Hurley et al., 2005; Clerbaux et al., 2007; Forster et al., 2007). C$_2$F$_6$ and C$_3$F$_8$ have lifetimes of at least 10,000 and 2600 years and GWP$_{100}$ of at least 12,200 and 8830, respectively (see Table 1).

Atmospheric CF$_4$ was first observed by Gassmann (1974) in krypton obtained by fractional air distillation. Soon CF$_4$ and C$_2$F$_6$ were found to be ubiquitous in the troposphere (Rasmussen et al., 1979; Penkett et al., 1981) and stratosphere (Goldman et al., 1979; Fabian et al., 1981). The less abundant C$_3$F$_8$ was just recently found in the atmosphere (Culbertson et al., 2000).

CF$_4$, and to a smaller degree C$_2$F$_6$, are released during primary aluminum (Al) production at the anode when the feed of aluminum oxide to the electrolysis cell is restricted ("anode effects") (Holliday and Henry, 1959; Penkett et al., 1981; Taberaux, 1994; International (Primary) Aluminium Institute, 1996, 2009b). Gassmann (1974) first suggested that there is also a natural CF$_4$ source based on mass spectrometric evidence in gas extracted from fluorite minerals by Kranz (1966). Harnisch et al. (1996a, 2000) and Harnisch and Eisenhauer (1998) found elevated CF$_4$ in fluorite and granite minerals and in Russian natural gas, pointing to a lithospheric source, and concluded that lithospheric emissions could explain the natural CF$_4$ background, even though anthropogenic fluxes were $10^3$–$10^5$ times higher and rising. Deeds et al. (2008) provided the first evidence for this lithospheric CF$_4$ flux based on dissolved CF$_4$ in groundwaters. From stratospheric profiles Fabian et al. (1987) concluded that natural sources contributed 43.5 ppt (parts per trillion) to the dry air mole fraction of atmospheric CF$_4$. Later Harnisch et al. (1996a, b) derived natural abundances of 39±6 ppt CF$_4$ from old air trapped in ice cores and glass vessels, and 44 ppt from stratospheric air dated by sulfur hexafluoride (SF$_6$) abundance. Khalil et al. (2003) estimated a natural abundance of 40–43.8 ppt CF$_4$ and Worton et al. (2007) obtained 34±1 ppt CF$_4$ from firn air. Despite this evidence of a large natural CF$_4$ abundance, some uncertainty in the correct value remained (Table 2). No natural C$_2$F$_6$ or C$_3$F$_8$ sources have been found (Harnisch, 2000) and natural abundances have been assumed to be insignificant (Fabian et al., 1987; Harnisch et al., 1996b; Khalil et al., 2003) or at most 0.3 ppt for C$_2$F$_6$ (Worton et al., 2007).

Since the 1980s CF$_4$, C$_2$F$_6$, and C$_3$F$_8$ have been used increasingly in semiconductor and other electronics manufacturing for cleaning, plasma etching, and chemical vapor deposition, leading to significant emissions due to incomplete conversion to fluorine plasma followed by release into the atmosphere (Cook, 1995; Victor and MacDonald, 1999; Harnisch, 2000; Tsai et al., 2002; Khalil et al., 2003). Khalil et al. (2003) and Worton et al. (2007) estimated the contributions from Al production and semiconductor/electronics manufacture to CF$_4$ and C$_2$F$_6$ emissions separately, but such detailed apportioning is difficult due to large uncertainties in the magnitude and temporal evolution of emission factors from Al production. Other potential anthropogenic sources, believed to be small, could include the production of fluorocarbons, fluorochemicals, and fluorine, the combustion of fluorocarbons and rocket fuels, the separation of uranium isotopes, and the use of fluororspar in steelmaking (Cicerone, 1979; Cook, 1995). So far no evidence for volcanic CF$_4$ emissions has been found (Rasmussen et al., 1979; Penkett et al., 1981; Symonds et al., 1988; Harnisch and Eisenhauer, 1998).

For the Northern Hemisphere (NH) Harnisch et al. (1995, 1996b, 1999) and Khalil et al. (2003) reconstructed CF$_4$ trends of ~1.1 ppt/yr from 1978 until ~1990 and reduced trends of ~0.7–1.0 ppt/yr thereafter, most likely caused by lower frequency and duration of "anode effects" due to measures by the Al industry to increase efficiency and to reduce PFC emissions (Taberaux, 1994; International (Primary)
Based on SF

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Table 2. Estimates of natural portions of accumulated atmospheric CF₄, C₂F₆, and C₃F₈.

<table>
<thead>
<tr>
<th></th>
<th>CF₄ (ppt)</th>
<th>C₂F₆ (ppt)</th>
<th>C₃F₈ (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>34.66±0.16 (Greenland)</td>
<td>0.1±0.02</td>
<td>&lt;0.02 (not detected)</td>
</tr>
<tr>
<td>This work</td>
<td>34.90±0.04 (Antarctica)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>34.7±0.2 (overall average)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Worton et al. (2007)</td>
<td>34±1</td>
<td>&lt;0.3</td>
<td></td>
</tr>
<tr>
<td>Khalil et al. (2003)</td>
<td>40, 43.8</td>
<td>all anthropogenic</td>
<td>all anthropogenic</td>
</tr>
<tr>
<td>Harnisch et al. (1996b)</td>
<td>~44</td>
<td>all anthropogenic</td>
<td></td>
</tr>
<tr>
<td>Harnisch et al. (1996a)b</td>
<td>39±6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fabian et al. (1987)b</td>
<td>~43.5</td>
<td>all anthropogenic</td>
<td></td>
</tr>
</tbody>
</table>

a Eleven air samples extracted from ancient Greenland ice (~11–19 kyr BP) and two old firn samples from Antarctica (~1910) were measured.

b Based on SF₆ dated stratospheric air.

c Khalil et al. (2003) scaled data by 0.8 to agree with the MPAE 86 scale. SH rise rate based on an error weighted linear fit of the Khalil et al. (2003) data.

d Based on air extracted from firn in the NH and SH and a firn model Worton et al. (2007) report a global doubling (from 40 to 78 ppt) from 1955 to 2003.

e See also Culbertson et al. (2000).

Note that Aoki and Makide (2004) reported excellent precision of ~1% for tropospheric CF₄ measurements based on CF₄/⁸⁰Kr ratios, but the method is complicated due to uncertainties in the tropospheric ⁸⁰Kr abundance (see Sect. 4.1.1).

Aluminium Institute, 1996, 2009b). For the Southern Hemisphere (SH) a general increase in CF₄ has also been shown, but measurements were sparser and uncertainties were larger (Table 3). Corresponding stratospheric increases in CF₄ were observed (Zander et al., 1996; Zhou et al., 1998; Rinsland et al., 2006). Small C₂F₆ increases before the 1980s were reconstructed by Worton et al. (2007) from firn air measurements, followed by a strong increase to ~0.07–0.09 ppt/yr from the 1980s to the early 2000s (Harnisch et al., 1995; 1996b; Khalil et al., 2003; Worton et al., 2007) (Table 4), probably due to increased emissions from the semiconductor industry and Al production. For C₃F₈ continuously increasing tropospheric trends from the 1970s to the mid-1990s have been reported, probably due to increasing use in the semiconductor industry (Khalil et al., 2003; Culbertson et al., 2004) (Table 5), but the scatter in the measurements is large.
For CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>, several sink processes have been investigated, including photolysis by vacuum ultraviolet radiation, reactions with oxygen and hydrogen atoms, vibrationally excited OH, and ions in the stratosphere and above. It seems that the lifetimes are mainly limited by thermal destruction during high-temperature combustion at ground level (Cicerone, 1979; Ravishankara et al., 1993; Morris et al., 1995). Similar sinks can be expected for C<sub>3</sub>F<sub>8</sub>. Due to their long atmospheric lifetimes, PFC emissions can permanently alter the radiative budget of the atmosphere (Cicerone, 1979; Abrahamson, 1992; Victor and MacDonald, 1999), and careful atmospheric long-term observations are necessary to quantify emissions.

Khalil et al. (2003) addressed substantial differences in the calibration scales of up to 20% for CF<sub>4</sub> and 64% for C<sub>2</sub>F<sub>6</sub> by multiplying their own and several other published CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> data sets by factors to bring them into reasonable agreement with data on the MPAE 86 calibration scale (e.g., Harnisch et al., 1995, 1996b, 1999). Moreover, the MPAE 86 and other PFC scales have stated uncertainties of ~±10% (Tables 3, 4, and 5), compared to 1–2% typically achieved for other halogenated trace gases (e.g., Maiss et al., 1996; Prinn et al., 2000). For CF<sub>4</sub>, the most abundant PFC, substantial analytical difficulties have prevented precisions better than several percent until now (Fig. 1, Table 3), compared to 0.04–0.5 ppt accuracy for CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>. Khalil et al. (2003) addressed this problem by developing analytical difficulties that allowed for more precise CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>F<sub>8</sub> measurements, resulting in improved accuracies of ~±1% compared to ~±10% (MPAE 86) for stratospheric measurements. Similar sink processes can be expected for C<sub>3</sub>F<sub>8</sub>, with substantially improved accuracies for CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>F<sub>8</sub> compared to other halogenated trace gases (e.g., Maiss et al., 1996; Prinn et al., 2000).

Here we present measurements of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>F<sub>8</sub> with significantly improved accuracies of ~1–2% on calibration scales developed for the Advanced Global Atmospheric Gases Experiment (AGAGE) program using new instrumentation which achieves excellent precisions for all three PFCs. We determine long-term baseline growth rates and interhemispheric gradients for CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>F<sub>8</sub> over three decades, based on measurements of the Cape Grim Air Archive (CGAA) for the Southern Hemisphere, archived air samples from various sources for the Northern Hemisphere, and several years of continuous atmospheric measurements at five remote AGAGE stations. The pre-industrial atmospheric Gases Experiment (AGAGE) program.
background of CF$_4$ is determined precisely from air extracted from Greenland ice and Antarctic firn. Global inversions of these measurements with the AGAGE 2-D 12-box model are used to estimate the global source strength of CF$_4$, C$_2$F$_6$, and C$_3$F$_8$ over the last three decades. We compare these measurement-based, top-down global source strengths with previous emission estimates and reveal significant discrepancies, underlining the need for more accurate, transparent, and complete emission reporting and verification with atmospheric measurements.

2 Experimental methods

2.1 Instrumentation and calibration

CF$_4$, C$_2$F$_6$, C$_3$F$_8$, and $\sim$35 other halogenated compounds are measured by AGAGE in 2L air samples with the “Medusa” cryogenic preconcentration system with gas chromatograph (GC, Agilent 6890) and quadrupole mass selective detector (MSD, Agilent 5973) (Miller et al., 2008). For this work, data from seven Medusa GC/MSD instruments were used. The instrument at the Scripps Institution of Oceanography (SIO, La Jolla, 33°N, 117°W, California) serves as the primary calibration instrument for the AGAGE network. Archived air samples (see Sect. 2.2) were measured at SIO and at the Commonwealth Scientific and Industrial Research Organisation Marine and Atmospheric Research (CSIRO, Aspendale, Australia). Routine ambient C$_2$F$_6$ and C$_3$F$_8$ measurements began in October 2003 at SIO, in November 2003 (C$_3$F$_8$) and January 2004 (C$_2$F$_6$) at the remote AGAGE stations Mace Head (MHD, 53°N, 10°W, Ireland), in January (C$_3$F$_8$) and April 2004 (C$_2$F$_6$) at Cape Grim (CGO, 41°S, 145°E, Australia), in April 2005 at Trinidad Head (THD, 41°N, 124°W, California), in May 2005 at Ragged Point (RPB, 13°N, 59°W, Barbados), and in May 2006 at Cape Matatula (SMO, 14°S, 171°W, American Samoa). Due to initial experimental difficulties from carbon dioxide interference, CF$_4$ data are used starting in April (THD), May (CGO, MHD), and June 2006 (RPB, SMO). Each sample was alternated with a reference gas analysis (Prinn et al., 2000; Miller et al., 2008), resulting in up to 12 fully calibrated samples per day. The reference gases at each site were calibrated relative to parent standards at SIO. Details of the calibration chain are reported in Miller et al. (2008).

CF$_4$ is reported on the SIO-2005 scale, C$_2$F$_6$ and C$_3$F$_8$ on the SIO-2007 scale, as parts per trillion (ppt) dry air mole fractions. All are based on volumetric halocarbon/nitrous oxide (N$_2$O) mixtures via a stepwise dilution technique with large dilution factors for each step ($10^2$ to $10^5$) (Prinn et al., 2000, 2001). The SIO-2005 CF$_4$ scale is based on four mixtures in artificial air with prepared values of 83.77–84.74 ppt. The SIO-2007 C$_2$F$_6$ and C$_3$F$_8$ scales are based on 4 and 5 mixtures with prepared values of 4.19–4.21 ppt C$_2$F$_6$ and 2.27–2.61 ppt C$_3$F$_8$, respectively, each containing $\sim$20 torr water vapor. The pure CF$_4$ (99.997%, Aldrich), C$_2$F$_6$ (99.99%, SynQuest Laboratories), C$_3$F$_8$ (>99.9%, SynQuest Laboratories), and N$_2$O (99.99%, Matheson) were further purified by repeated cycles of freezing ($\sim$196°C), vacuum removal of non-condensable gases, and thawing. Artificial air (Ultra Zero Grade, Airgas) was further purified via an absorbent trap filled with glass beads, Molecular Sieve (MS) 13X, charcoal, MS 5A, and Carboxen 1000 at $-80^\circ$C (ethanol/dry ice). Each zero air sample was measured to verify insignificant halocarbon blank levels before being spiked with the halocarbon/N$_2$O mixtures.

Due to the high volatility of CF$_4$ and the residual vapor pressure of 0.04 mbar at liquid nitrogen (N$_2$(l)) temperature (Lide, 1993, 2003) the transfer order of N$_2$O and halo-carbon to the stainless steel mixture canister had to be reversed for CF$_4$ compared to the method described in Prinn et al. (2000) to minimize the volume into which CF$_4$ expands and to minimize the size of the correction needed for the residual CF$_4$ vapor. The accurately measured bootstrap N$_2$O was first vacuum-transferred to the mixture canister by immersing it into N$_2$(l). Thereafter, the mixture canister and the attached capillary breaker were separated from the vacuum line and the calibrated volume (initially containing the measured N$_2$O). Then CF$_4$ was released from the capillary breaker, so that it equilibrated only with the capillary breaker ($\sim$13.48 ml±0.02%) and the N$_2$O filled mixture canister ($\sim$850 ml), but not with the large volume of the vacuum line. This way the only correction was for the small residual CF$_4$ vapor in the capillary breaker ($\sim$0.02%). Systematic uncertainties are conservatively estimated at $\sim$1–2%, see also Prinn et al. (2000). The SIO-2005 scale agrees with a CF$_4$ calibration by the National Institute for Environmental Studies (NIES) in Japan (Y. Yokouchi, personal communication, 2005) within 1.3% and with a dilution at SIO of a commercial gravimetric CF$_4$/CFC mixture (Linde, UK) within 0.08%.

CF$_4$ is monitored on its base (most abundant) ion, with a mass over charge ratio (m/z) of 69, and m/z 50 is used as a qualifier ion. C$_2$F$_6$ is monitored on m/z 119 for which interference is much less likely than for its base m/z 69 which is used as a qualifier. Similarly C$_3$F$_8$ is monitored on m/z 169 due to interference on its base m/z 69. Typical daily precisions of reference gas measurements are 0.05–0.2 ppt (0.06–0.3%) for CF$_4$, 0.02–0.06 ppt (0.5–1.5%) for C$_2$F$_6$, and 0.007–0.02 ppt (1.5–4.5%) for C$_3$F$_8$ at all sites. Typical precisions for archived air samples (see next section) were $\sim$0.08 ppt for CF$_4$, $\sim$0.03 ppt for C$_2$F$_6$, $\sim$0.01 ppt for C$_3$F$_8$, with 3–4 replicates for most older and 10–12 for most newer samples. Replicate analyses of NH archived air samples (see next section) over 2.5–4 years typically agree with precisions of less than 0.1 ppt for CF$_4$, 0.04 ppt for C$_2$F$_6$, and 0.01 ppt for C$_3$F$_8$, showing that the PFCs are stable. Replicate analyses of SH archived air samples during the measurements of the Cape Grim Air Archive (CGAA, see next section) at CSIRO typically agree with precisions of less than 0.1 ppt for CF$_4$, 0.02 ppt for C$_2$F$_6$, and 0.006 ppt for C$_3$F$_8$. Detection
The analytical systems showed no CF$_4$ blanks. At SIO, small C$_2$F$_6$ and C$_3$F$_8$ blanks were observed due to impurity of the helium carrier gas. This carrier gas blank was carefully assessed for each helium tank. If the blank variability was negligible, all measurements made using a particular carrier gas tank were blank corrected to remove non-linearity effects, otherwise measurements with variable and high blank were rejected. The resulting uncertainties due to the blank level variability are negligible compared to the overall precisions for C$_2$F$_6$ and C$_3$F$_8$. The linearity of the Medusa GC/MSD system used for the measurements of archived air from the SH (CGAA, see next section) was assessed with a series of diluted air samples (3.7–57 ppt CF$_4$, 0.3–3.4 ppt C$_2$F$_6$, and 0.02–0.34 ppt C$_3$F$_8$). For CF$_4$ and C$_2$F$_6$ no corrections were necessary, but for C$_3$F$_8$ a non-linearity correction of $\sim$6% (0.003 ppt) had to be applied for the oldest samples – however this correction is so small for these low abundances that the corrected and uncorrected results for most samples still agree within measurement precisions.

2.2 Archived air samples of the Northern and Southern Hemisphere

To reconstruct the atmospheric history of CF$_4$, C$_2$F$_6$, and C$_3$F$_8$, 124 unique archived Northern Hemisphere (NH, 1973–2008) air samples were measured at SIO, and 64 unique archived Southern Hemisphere (SH, 1978–2006) air samples from the Cape Grim Air Archive (CGAA) (Krummel et al., 2007) were measured at CSIRO. Six additional SH samples with fill dates ranging from 1995 to 2004 were measured at SIO. For CF$_4$ and C$_2$F$_6$ all six samples were in excellent agreement with the SH samples with similar fill dates measured at CSIRO (delta mole fraction $\Delta x=0.01–0.17$ ppt CF$_4$, $\Delta x=0.02–0.03$ ppt C$_2$F$_6$). For C$_3$F$_8$ one sample was rejected as an outlier with lower than expected C$_3$F$_8$ mixing ratios ($\Delta x=0.04$ ppt). Similarly, five additional NH samples with fill dates ranging from 1980 to 1999 were measured at CSIRO. For CF$_4$ and C$_2$F$_6$ three of the five samples were in excellent agreement with the NH samples with similar fill dates measured at SIO (delta mole fraction $\Delta x=0.07–0.13$ ppt CF$_4$, $\Delta x=0.01$ ppt C$_2$F$_6$, $\Delta t=0–9$ days). For C$_3$F$_8$ four of the five samples were in excellent agreement ($\Delta x=0.011$ ppt C$_3$F$_8$). For one of the NH samples measured at CSIRO the corresponding NH sample with similar fill date measured at SIO was rejected as an outlier with lower than expected CF$_4$ and C$_2$F$_6$ mixing ratios ($\Delta x=1.13$ ppt CF$_4$, $\Delta x=0.02–0.03$ ppt C$_2$F$_6$).

Fig. 1. AGAGE CF$_4$ abundances from archived Northern Hemisphere (NH) and Southern Hemisphere (SH) air samples and in situ measurements at Mace Head, Ireland (NH), Trinidad Head, California (NH), and Cape Grim, Tasmania (SH) and modeled 30–90° N and 30–90° S abundances all shown on the SIO-2005 calibration scale compared to previous observations. Uncertainty estimates for the SIO-2005, MPAE 86, and UEA calibration scales are indicated as additional dashed error bars.
of errors in the model parameters, including errors in inter-

tors (EF, kg PFC/tonne Al produced). Emissions during

3. Modeling studies

3.1 Two-Dimensional 12-box model

A 2-D 12-box chemical transport model was used to simulate
time-varying monthly background semi-hemispheric abun-
dances in eight tropospheric and four stratospheric boxes,
with horizontal divisions at the poles, ±30° and at the equa-
tor and with vertical divisions at 1000, 500, 200 and 0 hPa.
Measured abundances were compared to the four surface
model boxes. The model uses zonally averaged velocities
and parameterized diffusion coefficients that exhibit seasonal
variation but are annually repeating. This 2-D model has
been used successfully in several previous studies to simu-
late the zonally averaged behavior of gases with lifetimes
that are long compared to the interhemispheric exchange time
and that show no sharp emissions changes (Cunnold et al.,
1983, 1994, 2002). The PFCs, with lifetimes of thousands of
years (Table 1), clearly satisfy this requirement. The compu-
tational efficiency of the 2-D model allows for calculation of
model parameter errors and the resulting uncertainties in the
inversion.

3.2 Inversion approach for CF$_4$, C$_2$F$_6$, and C$_3$F$_8$

Annual emissions were deduced for the four semi-
hemispheres using an approach based on a Bayesian dis-
crete recursive weighted least squares filter (Prinn, 2000).
The unknowns were annual emissions from 1973–2009 for
each of the four semi-hemispheres. “Pulses” of emissions
were released sequentially for each year and in each semi-
hemisphere and the resulting mole fractions were tracked
through the model to estimate the time-varying sensitivity of
the mole fractions in each box to annual emissions from each
source region. Given these sensitivities, the filter was used to
combine information between a prior “guess” of the emis-
sions and information from each measurement, weighted
by their uncertainties. Total uncertainties include those de-
derived from the filter as well as an estimate of the influence of
errors in the model parameters, including errors in inter-
hemispheric and stratosphere-troposphere mixing times.

Initial estimates of PFC emissions prior to the earliest sam-
ple date (1973) of air measured by AGAGE were determined
using primary Al production from 1900–1972 (US Geologi-
cal Survey, 1932–2009) multiplied by constant emission fac-
tors (EF, kg PFC/tonne Al produced). Emissions during
this period were required to spin up the model from a glob-
ally well-mixed atmosphere in 1900, in which pre-industrial
mole fractions were assumed. EFs were derived from 1973
PFC emissions in the EDGAR v4 emission database (2009)
for CF$_4$ and C$_2$F$_6$ and from preliminary measurements in

www.atmos-chem-phys.net/10/5145/2010/
an Australian Al smelter for C\textsubscript{3}F\textsubscript{8} and scaled throughout this model spin-up period using the 1973 emissions derived from the inversion, resulting in 1.14 kg CF\textsubscript{4}/tonne Al, 0.117 kg C\textsubscript{2}F\textsubscript{6}/tonne Al, and 0.0055 kg C\textsubscript{3}F\textsubscript{8}/tonne Al. As we have not measured any air collected prior to 1973, the temporal evolution of the emission factors before 1973 could not be determined. We assumed a 30% uncertainty for the 1973 EDGAR v4 (2009) emissions and set an initial semi-hemispheric distribution using 1970 EDGAR 32/FT2000 gridded data (Olivier and Berdowski, 2001) due to lack of 1970 EDGAR v4 gridded data.

EDGAR v4 and other previous estimates are substantially different from emissions derived from AGAGE measurements and their use as independent “prior” emissions in the inversion led to unduly biased inversion results. Therefore, the approach was modified so that after 1973, “prior” emissions for each year were assumed to be the emissions from the previous year with a 1σ uncertainty of 5% for CF\textsubscript{4} and C\textsubscript{2}F\textsubscript{6} and 20% for C\textsubscript{3}F\textsubscript{8}. These constraints on emission changes were included in the inversion to avoid unrealistically large emission changes. They were consistent with the expected rate of change of emissions, based on the maximum rate of change of the mixing ratio growth during each time series. To account for the low frequency of archive data, this was achieved by fitting a sixth order polynomial and finding the maximum of the second derivative and normalizing to the growth rate to find the fractional change in emissions.

The structure of the emissions vector, \textit{x}, and error covariance matrix, \textit{P}, are shown in Eqs. (1–2). \textit{x} contains sub-vectors of emissions \textit{q} for year \textit{i}, with each \textit{q} containing emissions from the four semi-hemispheres. Similarly, each element in \textit{P} is a sub-matrix with errors from the four semi-hemispheres. The diagonal elements, \sigma\textsuperscript{2}_{ii}, of the error covariance matrix, contain the square of emissions errors in year \textit{i}, while the off-diagonal terms correspond to errors from spatial and temporal correlations. Initially all annual emissions were assumed to be uncorrelated.

An estimate of the emissions time series was made by sequentially incorporating measurements at time-step \textit{k} and updating the emissions vector and error covariance matrix as shown by Eqs. (3–5). Superscripts \textit{f} and \textit{a} refer to forecasted and analyzed values. \textit{H}_k is a Jacobian matrix describing the sensitivity of mole fractions to changes in emissions, \textit{y}_{k}\textsuperscript{0} and \textit{y}_k refer to observed and simulated mole fractions, respectively, and \textit{R}_k is the measurement covariance matrix, with diagonal elements equal to the square of the measurement error.

\begin{align*}
\textit{x}_k^f &= [q_1,q_2,...,q_{37}]^T \quad \text{(1)} \\
\textit{P}_k^f &= \begin{bmatrix}
\sigma_{11}^2 & 0 & \cdots & 0 \\
0 & \sigma_{22}^2 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & \sigma_{37,37}^2
\end{bmatrix} \quad \text{(2)}
\end{align*}

\begin{align*}
\textit{x}_k &= \textit{K}_k (\textit{y}_k^0 - \textit{y}_k) + \textit{x}_k^f \\
\textit{P}_k &= (\textit{I} - \textit{K}_k \textit{H}_k)\textit{P}_k^f \\
\textit{K}_k &= \textit{P}_k^f \textit{H}_k^T (\textit{H}_k \textit{P}_k^f \textit{H}_k^T + \textit{R}_k)^{-1}
\end{align*}

To begin, the first measurement (at \textit{k}=0) was incorporated, leading to an update of the emissions vector and covariance matrix. Only the first element was updated, since there is no sensitivity to future emissions. Next, emissions were forecasted for the second year to be the same as the current emission estimate from the first year (first year emissions could still be updated as more measurements were incorporated), \pm the expected maximum growth rate. The entire emissions vector was then updated through Eqs. (3–5) by incorporating the second measurement, leading to a new estimate of the emissions vector and error covariance matrix. This process was used for the thirty-seven year period in the inversion. Monthly measurements were used, when available, to update annual emissions which were assumed to be constant over the year.

Measurement uncertainties were calculated as the square root of the sum of the squared errors resulting from sampling frequency, measurement-model mismatch, instrument precision, and scale propagation. Sampling frequency error characterizes the uncertainty that arises from using a finite number of measurements to define a time-varying monthly mean mixing ratio and was estimated as the square root of the ratio of the monthly mean baseline variability to the number of measurements. Since the monthly mean variance was only known at high-frequency stations, it was defined for flask measurements as having the same variance as at the high-frequency stations in the same semi-hemisphere, scaled by the mean mole fraction. Mismatch error is associated with how well the point measurements represent the background, semi-hemispheric mole fractions assumed in the model. It was estimated here as equal to the scaled variability of the high-frequency station in the same latitude band as the archived air measurements, and reflects the inability of the model to account for spatial gradients within each semi-hemisphere. Precisions are specific to each gas, as discussed below, and are inversely scaled with the square root of the number of measurements. Scale propagation error is associated with calibration tank changes and calibration scale propagation. It was estimated as equal to the precision error but independent on the number of measurements.

4 Results and discussion

4.1 Atmospheric records spanning more than 30 years in each hemisphere

The atmospheric histories of CF\textsubscript{4}, C\textsubscript{2}F\textsubscript{6}, and C\textsubscript{3}F\textsubscript{8} in the SH shown in green colors in Figs. 1, 2, and 3 were reconstructed from analysis of archived SH air from the Cape
The atmospheric histories in the NH shown in blue colors in Figs. 1, 2, and 3 were reconstructed from analysis of archived NH air (mostly from Trinidad Head and La Jolla, California [SIO samples and also from Point Barrow, Alaska [UCB samples], Niwot Ridge, Colorado [NOAA/GMD and CSIRO samples], Cape Meares, Oregon [NOAA/GMD, NILU, and CSIRO samples, originally collected by R. A. Rasmussen, Oregon Graduate Institute (OGI)], and Harvard Forest, Massachusetts [SIO samples]) and background monthly mean in situ data for Trinidad Head, California and Mace Head, Ireland. The combined data yield records spanning more than 30 years for each PFC in both hemispheres. Archived air and in situ data agree very well during the overlap periods for all three PFCs in the NH and for C$_2$F$_6$ in the SH. For C$_3$F$_8$ some SH archive samples are slightly elevated but in 2005 and 2006 the agreement is excellent. For CF$_4$ there is no overlap period, but a continuous transition occurred without any apparent steps. The start times of in situ measurements for each compound at each site are provided in Sect. 2.1. For details on archived air samples see Sect. 2.2. This degree of agreement, as well as the results of the tests described in Sect. 2.2 document that the Medusa GC/MSD instruments and calibration methods result in highly consistent data sets. The AGAGE PFC data sets for the NH start five years earlier and end eleven to twelve years later than previously reported data sets of direct PFC measurements in air samples (Harnisch et al., 1999; Khalil et al., 2003; Culbertson et al., 2004). The lengths of the AGAGE PFC data sets in the SH are unique.

### 4.1.1 CF$_4$ measurements

The precision of our AGAGE CF$_4$ data, <0.3%, or <0.2 ppt (Fig. 1), is substantially improved compared to previous methods (typically ~5%, or a few ppt, Fig. 1 and Table 3). Together with the high integrity of both the archived air samples and the in situ data, this precision leads to well-defined abundances and rise rates in both hemispheres (Fig. 1 and Table 3) with the first clearly defined interhemispheric gradients. CF$_4$ rise rates were ~1.07 ppt/yr until ~1991 and ~0.7 ppt/yr since ~1993, similar to previous reports but better constrained (Table 3). A decrease of the CF$_4$ rise rate is clearly evident between ~1991 and ~1994, mostly likely due to increased efficiency of the Al industry and resulting reduced emissions as reported by the International (Primary) Aluminium Institute (1996, 2009a).

The estimated uncertainty of AGAGE CF$_4$ data on the SIO-2005 CF$_4$ scale is at ~1–2% (Fig. 1) less than the ~10% stated uncertainty for the widely used MPAE 86 (Max Planck Institute for Aeronomy) calibration scale (Fabian et al., 1996; Harnisch et al., 1996b, 1999) and the ~10 ppt, or 13.9% for the UEA (University of East Anglia) calibration scale (Worton et al., 2007) (Fig. 1, Table 3). As described in Sect. 2.1, the accuracy estimate of the SIO-2005 scale is supported by the good agreement with two independent CF$_4$ calibration mixtures.

The CF$_4$ abundances reported here are 6–10% lower than those in previous reports. Background tropospheric mixing ratios increased from ~49.9 ppt in 1978 to ~76.9 ppt at the end of 2008 in the SH and from ~46.3 ppt in 1973 to ~78.0 ppt at the end of 2008 in the NH. Previous data with MPAE 86 and UEA calibrations actually are consistent with our AGAGE observations when calibration uncertainties are taken into account. This also applies to data presented by Khalil et al. (2003) which were scaled to agree with the MPAE 86 calibration.

Aoki and Makide (2004) recently used an independent calibration and measurement approach and reported $80.7 \pm 0.6$ ppt CF$_4$ in one air sample taken in Tokyo on 9 August 2003 (Fig. 1), which is ~1.5 ppt higher than an extrapolation of previous data with MPAE 86 and UEA calibrations. Instead of measuring CF$_4$ directly, they measured the CF$_4$/$^{80}$Kr ratio to circumvent the substantial matrix and separation problems associated with the inevitable co-trapping of CF$_4$ and major atmospheric constituents. They used $^{80}$Kr as an internal standard, relying on the precise knowledge of its atmospheric abundance, its uniform distribution, and the assumption that it behaves similarly to CF$_4$ during trapping and separation. Later Aoki and Makide (2005) revised the atmospheric $^{80}$Kr abundance, which would lead to $77.8 \pm 0.6$ ppt CF$_4$, ~3 ppt lower than reported in 2004. In addition to these uncertainties, it might not be possible to measure reliable CF$_4$ background values in a single Tokyo air sample as several significant CF$_4$ sources are nearby according to the EDGAR 32/FT2000 emission database (Olivier and Berdowski, 2001).

### 4.1.2 C$_2$F$_6$ measurements

The precision of our AGAGE C$_2$F$_6$ data and the quality of the archived air measurements are improved compared to most previously reported C$_2$F$_6$ data sets, and abundances in both hemispheres are more clearly defined (Table 4, Fig. 2). It is possible to quantify consistent interhemispheric gradients for the first time, which are clearly larger than those suggested by Khalil et al. (2003) and Worton et al. (2007). Tropospheric mixing ratios increased from ~0.96 ppt in 1978 to ~3.93 ppt at the end of 2008 in the SH and from ~0.75 ppt in 1973 to ~4.06 ppt at the end of 2008 in the NH. The SH rise rates were ~0.087 ppt/yr until ~1997 (similar to previously published NH rise rates), followed by a faster increase of ~0.119 ppt/yr until ~2004, and a slower increase of ~0.099 ppt/yr thereafter. The NH C$_2$F$_6$ data show similar trends, but it is difficult to calculate actual rise rates due to larger scatter. Trend changes may have been caused by a combination of changing emissions from the Al industry, a sharp increase of emissions after the introduction of C$_2$F$_6$ as a fluorine source in semiconductor/electronics manufacture.
The SIO-2007 calibration scale uncertainty estimate for the AGAGE C$_2$F$_6$ abundances all shown on the SIO-2007 scale compared to previous observations. The SIO-2007 calibration scale uncertainty estimate (~1–2%) is similar to the shown precisions.

This work
- NH tanks
- THD monthly mean
- MHD monthly mean
- SH tanks
- COO monthly mean

Other published work
- Worton et al., 2007 NH + SH
- Khalil et al., 2003 NH, SH
- Culbertson et al., 2000 NH
- Hamisch et al., 1996b
- Fabian et al., 1987, 1996
- Penkett et al., 1981 NH + SH

AGAGE C$_3$F$_8$ abundances from archived Northern Hemisphere (NH) and Southern Hemisphere (SH) air samples and in situ measurements at Mace Head, Ireland (NH), Trinidad Head, California (NH) and Cape Grim, Tasmania (SH) and modeled 30–90° N and 30–90° S abundances all shown on the SIO-2007 scale compared to previous observations. The SIO-2007 calibration scale uncertainty estimate (~1–2%) is similar to the shown precisions.
in the early 1990s as indicated by the EDGAR v4 emission database (2009), followed by a gradual replacement of C$_2$F$_6$ with more efficient fluorine sources such as nitrogen trifluoride (NF$_3$, Air Products, personal communications, 2009) (Weiss et al., 2008) and possibly improved abatement of C$_2$F$_6$ emissions. C$_2$F$_6$ mixing ratios and rise rates in the NH reported by Khalil et al. (2003) and Harnisch et al. (1996b) mostly agree with our AGAGE data, but C$_2$F$_6$ mixing ratios reconstructed from firn air by Worton et al. (2007) differ significantly and show different trends.

4.1.3 C$_3$F$_8$ measurements

The precision of our AGAGE C$_3$F$_8$ data is similar to the C$_3$F$_8$ precisions of Khalil et al. (2003) and Culbertson et al. (2004), but our NH abundances are lower (Fig. 3, Table 5), especially before ~1983, and the rise rates are different. Tropospheric mixing ratios increased from ~0.05 ppt in 1978 to ~0.5 ppt at the end of 2008 in the SH and from ~0.02 ppt in 1973 to ~0.52 ppt at the end of 2008 in the NH. Rise rates are more difficult to define than for CF$_4$ and C$_2$F$_6$, especially in the NH. They were ~0.0062–0.0066 ppt/yr in both hemispheres from the mid-1970s to the early/mid-1990s, followed by a steep increase to ~0.024 ppt/yr until ~2000/2001, and a possible further increase to ~0.033 ppt/yr in the SH (2001–2004). Rise rates returned to ~0.024 ppt/yr shortly thereafter (SH: 2004–2008, NH: 2003–2007), and declined to ~0.015 ppt/yr in the NH recently (2007–2008). Without detailed information about industrial production and resulting emissions of C$_3$F$_8$ one can only speculate that early emissions were from Al production (Harnisch et al., 1998) and that the recent large increase in emissions is due to semiconductor/electronics manufacture and refrigeration/air conditioning use (see Sect. 5.4).

4.2 Pre-industrial abundances of CF$_4$, C$_2$F$_6$, and C$_3$F$_8$

We measured 34.66±0.16 ppt CF$_4$ in the ancient Greenland air samples and 34.90±0.04 ppt in the oldest (~1910) Antarctic firn air samples. There is only a very small difference between these two results, leading to a significantly better defined pre-industrial CF$_4$ abundance with an overall average of 34.7±0.2 ppt (Table 2). As expected from the calibration differences for modern data, most previously reported pre-industrial estimates were higher. However, Worton et al. (2007) present a similar pre-industrial CF$_4$ abundance of 34±1 ppt, derived from an extrapolation of CF$_4$ and C$_2$F$_6$ firn data dated with a firn model to zero C$_2$F$_6$ abundance assuming no natural C$_2$F$_6$. This agreement is difficult to interpret, because the C$_2$F$_6$ mixing ratios at the beginning of the Worton et al. (2007) record are higher compared to AGAGE, the curvatures of the C$_2$F$_6$ abundances differ, and the CF$_4$ calibration scales differ significantly (Figs. 2 and 3).

We measured 0.1±0.02 ppt C$_2$F$_6$ in the lowest Megadunes firn sample. It is conceivable that this pre-industrial, back-ground C$_2$F$_6$ level represents evidence for a small lithospheric source, as found for CF$_4$ by Deeds et al. (2008). C$_3$F$_8$ was below our detection limit.

5 Global emission estimates from air archive and in situ measurements

The global top-down emissions derived with the AGAGE 2-D 12-box model (Sects. 3.1 and 3.2) are shown in Figs. 4, 5, and 6, for CF$_4$, C$_2$F$_6$, and C$_3$F$_8$, respectively, together with other published top-down and bottom-up emission estimates. The inversions are based on our archive and in situ real-time measurements from five remote AGAGE stations and the measured pre-industrial, natural backgrounds for CF$_4$ and C$_2$F$_6$ discussed above. Significant error reductions of the emissions were achieved during the inversion in all model boxes when in situ high-frequency data were available (2006–2009) and in the 30–90°N box for all years. From 2006–2009 the semi-hemispheric emissions for all PFCs were clearly uncorrelated ($R^2<0.1$). However, before 2006 insufficient information was available to reduce the error significantly for semi-hemispheric scale emissions. Compared to the global estimates, semi-hemispheric emissions may be more sensitive to model transport parameter uncertainties and inter-annual transport variations, but the influence of these limitations are accounted for in the uncertainties of the derived emissions by including model parameters uncertainties in the error analysis. Global emissions are plotted as 5-year moving averages until 1985, 3-year moving averages from 1986 to 1999, followed by yearly values, to avoid physically unreasonable emission changes due to the variable data density. Residuals of modeled minus observed mixing ratios are generally smaller than the measurement uncertainty (shown in Fig. S3) indicating that the derived emissions are consistent with the atmospheric measurements. Residuals that lie outside of the measurement uncertainty may have occurred when the sampled air was not truly representative of the semi-hemispheric background.

5.1 CF$_4$ emissions

AGAGE global top-down CF$_4$ emissions (Fig. 4) were ~15 Gg/yr in 1975, rising to ~18 Gg/yr around 1980, generally declining to ~11 Gg/yr in 2000, and stabilizing at ~11 Gg/yr thereafter. While Harnisch et al. (1995, 1996b, 1999) report similar top-down averaged emissions before 1996, Khalil et al. (2003) estimate slightly lower average top-down emissions, and Worton et al. (2007) report substantially lower emissions before the mid-1990s (Table 6). Similarly, CF$_4$ emissions reported before ~1991 by EDGAR v4 (2009) are significantly lower while their agreement with AGAGE top-down emissions is good from ~1991 to ~2005 (and until 2008 if extrapolated). It is important to note that EDGAR v4 does not simply use 2006
Intergovernmental Panel on Climate Change (IPCC) Guidelines to estimate CF$_4$ emissions from Al production, but that EDGAR v4 CF$_4$ emission factors, including their trend after 1985, have been selected to be compatible with bottom-up reporting to the UNFCCC and with previously published measured atmospheric trends (see http://edgar.jrc.ec.europa.eu/faq7.php#flu). In other words, EDGAR v4 CF$_4$ emissions are not pure bottom-up estimates, but rather a hybrid between bottom-up estimates and top-down interpretation of atmospheric measurements. It is unclear which atmospheric trends were used, but it seems likely that this explains the good agreement of EDGAR v4 with our AGAGE top-down emissions after ~1990, and the improved agreement before ~1991 compared to EDGAR 32/FT2000 (Olivier and Berdowski, 2001) (Table 6).

The 2006–2009 emissions distribution modeled from our AGAGE measurements is 92±2%, 6±2%, 1±0.4%, and 1±0.4% for the 30–90°N, 0–30°N, 0–30°S, and 30–90°S semi-hemispheres, respectively. EDGAR v4 estimates 80%, 11%, 8%, and 1% for the same semi-hemispheres, respectively, in 2005. If global AGAGE emissions are distributed according to EDGAR v4, the discrepancy between modeled and observed abundances are markedly higher, indicating that EDGAR v4 probably underestimates contributions from the NH.

Also shown in Fig. 4 are CF$_4$ emission estimates based on PFC emission data collected by the UNFCCC process (bottom-up) from the 34 Annex I reporting countries (United Nations Framework Convention on Climate Change, 2009, Supplement I and Table S1). These emissions have declined by more than a factor of two from 1990 (9.3 Gg) to 2006 (4.4 Gg). In 2006 they were less than half of the global ~11 Gg/yr AGAGE emission estimate. This is not surprising as the UNFCCC reporting Annex I countries account for a little over 50% of global Al production. Among non-Annex I countries that emit PFCs from Al production are China, Brazil, South Africa, India, United Arab Emirates and Bahrain, which together accounted for 40% of 2006 global Al production (US Geological Survey, 1932–2009), thus demonstrating the need for global reporting.

To validate the PFC emission reduction measures by the global aluminum industry under the auspices of the International (Primary) Aluminium Institute (IAI), IAI has estimated global Al production PFC emissions using data on smelting-technology-specific Al production and PFC (CF$_4$ and C$_2$F$_6$) bottom-up emission factors (EFs) and coefficients in their IAI Anode Effect surveys (1996, 2000, 2001, 2003–2008, 2009a, b). PFC measurements made at Chinese smelters in 2008 as part of the Asia Pacific Partnership for Clean Energy and Climate and seven additional measurements reported by the Aluminum Corporation of China Limited (CHALCO) found a median emission factor for smelters using PFPB (Point Feed PreBake) technology of 0.7 tonnes CO$_2$-equivalent (CO$_2$-e)/tonne Al produced, compared to the median performance of 0.27 tonnes CO$_2$-e/tonne Al from IAI global PFPB survey participants (IAI, 2009a), or ~2.6 times higher EF. Until the mid-2000s, Chinese Al production was dominated by Horizontal Stud Soderberg (HSS) technology, but through the mid-2000s a transformation occurred in the Chinese industry and by the end of 2005 the China Non-Ferrous Metals Industry Association (CNIA) reported that all smelters used PFPB technology. Global CF$_4$ emissions calculated from the IAI surveys increase by ~0.6–0.8 Gg/yr from 2006 to 2008 when the increased EF for Chinese smelters is taken into account (Supplement 2 and Table S2). The resulting corrected global Al production CF$_4$ emissions plotted in Fig. 4 are ~11.4 Gg/yr in 1990 and ~3.8 Gg/yr in 2006. When these updated IAI Al production CF$_4$ emission estimates are added to the EDGAR v4 non-metal production (mostly semiconductor/electronics manufacture) CF$_4$ emission estimates, the resulting global sum (Fig. 4) is substantially lower than AGAGE global top-down emissions, by ~3.7±1.1 Gg/yr from 1990 to 1992, by ~2.5±0.5 Gg/yr from 1998 to 2000, and by ~5.9±0.3 Gg/yr from 2003 to 2005. That is, the sum of available bottom-up CF$_4$ emission estimates is significantly lower than total global emissions as measured in the atmosphere.

One possible explanation for the growing emissions gap (~6.1 Gg/yr in 2005) is that the IAI still underestimates Al production CF$_4$ emissions from China which produced ~24% of global Al in 2005 (US Geological Survey, 1932–
2009) and ~34% in 2008 (IAI, 2009a) – even after applying the 2.6 times larger EF for Chinese smelters using PFPB. The observed emission gap of ~3.7±1.1 Gg/yr from 1990 to 1992, when China produced only ~4% of global Al (IAI, 2009a), could also indicate an inherent underestimation of Al production CF\(_4\) emissions calculated from the surveys, as might be explained by fundamental problems with the application of IPCC methodologies. Recently Maltais et al. (2010) discovered significant PFC emissions during the startup of reduction cells which may not be accounted for by IPCC methodology. Note that EDGAR v4 metal production CF\(_4\) emissions are significantly higher than emissions estimated from the IAI surveys, but as discussed above, it remains unclear how EDGAR v4 CF\(_4\) emissions have been estimated and to what degree they depend on previous atmospheric observations. Another possible explanation for the emission gap is that PFC emissions from semiconductor/electronics manufacture in EDGAR v4, including from China, are significantly underestimated. The World Semiconductor Counsel (WSC) reports that semiconductor manufacturers in Europe, Japan, US, Korea, China, and Taiwan pursue a voluntary perfluorocompound emission reduction program and that indexed perfluorocompound emissions have increased from 1995 to 2001 by ~60% and decreased slightly below 1995 values from 2001 to 2008 (http://www.sia-online.org/galleries/Publications/2009_WSC_Joint_Statement.pdf). However, the report lists only relative emissions, does not explain how they were measured, estimated, and/or verified, and gives no information how the emissions of specific perfluorocarbons such as CF\(_4\) or C\(_2\)F\(_6\) have evolved. The use of the phrase perfluorocompounds instead of perfluorocarbons suggests that SF\(_6\) and NF\(_3\) may be included in the sum which would further complicate the interpretation of the WSC data. Although there are indications that continuing technology upgrades and the shutdown of older facilities for semiconductor/electronics manufacture have led to a slow replacement of CF\(_4\) with more efficient fluoride sources such as NF\(_3\) (Air Products, personal communications, 2009) which would reduce CF\(_4\) emissions from semiconductor/electronics manufacture, there are no primary sources of data to support this conclusion, and it remains unclear how CF\(_4\) or C\(_2\)F\(_6\) emissions from the semiconductor/electronics industry are estimated in EDGAR v4.

Lastly, we find it is surprising that UNFCCC Annex I CF\(_4\) emissions from Al and non-Al sources agree so well with global Al production related CF\(_4\) emissions estimated from the IAI reports (Annex I and non-Annex I Al production). This would require Annex I non-Al based CF\(_4\) emissions to be large and comparable to non-Annex I Al based CF\(_4\) emissions.

### 5.2 C\(_2\)F\(_6\) emissions

AGAGE global top-down C\(_2\)F\(_6\) emissions (Fig. 5) were ~1.5 Gg in 1975, rising to ~2.2 Gg/yr during the early to mid-1990s, increasing to ~3 Gg/yr during the early 2000s, and decreasing to ~2.3 Gg/yr in 2008. Harnisch et al. (1995, 1996b) reported similar top-down emissions until the mid-1990s (2 Gg/yr, 1978–1995, 1.9 Gg/yr 1982–1996, see Table 7). Khalil et al. (2003) reported emissions similar to AGAGE until the mid-1980s (as the sum of 11.5% of Al production CF\(_4\) emissions and 70% of semiconductor CF\(_4\) emissions), after which they are lower by up to ~0.9 Gg/yr. Worton et al. (2007) estimate lower top-down C\(_2\)F\(_6\) emissions (Fig. 5) as expected from their lower reconstructed C\(_2\)F\(_6\) rise rate (Fig. 2).

While C\(_2\)F\(_6\) emissions in the EDGAR v4 emission database (2009) agree well with our AGAGE global top-down emissions before ~1992, in contrast to much
lower emissions in the older EDGAR 32/FT2000 emission database, C₂F₆ emissions after 1991 are lower in EDGAR v4 by ~0.5 Gg/yr. It is unclear why EDGAR v4 C₂F₆ emissions agree with AGAGE results before ~1992, while CF₄ emissions only agree after ~1990, especially as C₂F₆ emissions are often estimated as a constant fraction of CF₄ emissions. As is the case for CF₄, EDGAR v4 C₂F₆ emission estimates are a hybrid of bottom-up methodologies and top-down estimates based on previously published atmospheric measurements.

The 2006–2009 emissions distribution modeled from our data is 96±2%, 3±1%, 1±0.4%, and 1±0.2% for the 30–90° N, 0–30° N, 0–30° S, and 30–90° S semi-hemispheres, respectively. EDGAR v4 estimates a similar NH:SH ratio for 2005 with 76%, 21%, 3%, and ~1% for the same semi-hemispheres, respectively, but shifts emissions within the NH towards the tropics.

As with CF₄ emissions, estimated C₂F₆ emissions from UNFCCC data (Supplement 1, Table S1) are substantially lower than emissions based on AGAGE measurements. UNFCCC reported Annex I country emissions have declined by about 50% from ~1.4 Gg/yr in 1990 to ~0.8 Gg/yr in 2006, while AGAGE top-down emissions peaked in ~2000 at ~3 Gg/yr, and in 2006 were ~2.3 Gg/yr, similar to the 1990 value of ~2.2 Gg/yr. Again, the discrepancy is not surprising as non-Annex I countries with significant Al production (i.e., China, Brazil, South Africa, India, United Arab Emirates, Bahrain) and semiconductor/electronics manufacture (i.e., China, South Korea, Taiwan) are not included in the UNFCCC numbers, again demonstrating the need for global reporting.

Smelter technology-specific Al production emission ratios of C₂F₆/CF₄ (by mass) for 1990 and 2000 reported by IAI (2001; 2003) are similar and industrial average emission ratios were ~10% C₂F₆/CF₄ (by mass) in 1990 and 2000 (see IPCC 2000 methodology in Zhihong et al., 2001). IPCC 2006 methodology recommends similar technology-specific emission ratios, except for SWPB (Side Worked Prebake), which is used to a smaller extent than other technologies (Harnisch et al., 2006; International Aluminium Institute, 2009a). Assuming that the CF₄ and C₂F₆ abundances measured by AGAGE in the early 1970s air samples stem from Al production and the natural background only, we deduce an emissions ratio of 10.2% C₂F₆/CF₄ (by mass) from Al production. Lacking further information, we estimate later Al production C₂F₆ emissions by multiplying the Al production CF₄ emissions from the IAI Anode Effect surveys (Sect. 5.1) by this emission ratio. Resulting Al production C₂F₆ emissions (Fig. 5) are lower than or similar to EDGAR v4 emissions from metal production (mostly Al). When EDGAR v4 non-metal production C₂F₆ emissions (~97% from semiconductor/electronics manufacture) are added to our Al production C₂F₆ emission estimates, the sums are lower than our global AGAGE top-down emission estimates.

If the differences between global top-down AGAGE CF₄ emissions and the sums of Al production CF₄ emissions (IAI Anode Effect survey) and non-Al production emissions (EDGAR v4) were due to underestimated Al production CF₄ emissions, the estimate for Al production C₂F₆ emissions would need to be increased correspondingly by 10.2% (by mass) of the CF₄ difference. The resulting sum of Al and non-Al production C₂F₆ emissions would agree much better with AGAGE emissions from 2002 to 2005 (difference ~0.2 Gg/yr), but emissions from 1990 to 2001 would remain underestimated by ~0.4 Gg/yr, either because the assumptions are wrong and/or because EDGAR v4 semiconductor/electronics manufacture C₂F₆ emissions from 1990 to 2001 are also underestimated.

5.3 CF₄ and C₂F₆ equivalent CO₂ emissions

Recent IAI Anode Effect surveys report a sum of total CF₄ and C₂F₆ CO₂-equivalent (CO₂-e) emissions using IPCC 2001 Second Assessment Report (SAR) global warming potentials (100-yr GWPs, Table 1) rather than separate CF₄ and C₂F₆ emissions or emission factors. Since the 2006 IAI Anode Effect survey (2008) total CO₂-e emissions reported for 1990 and 1995 are ~10% higher than in previous surveys, due to the change from IPCC 2000 to IPCC 2006 methodology, but CO₂-e emissions reported for 2000, 2004, and 2005 remain very similar. Correspondingly the CO₂-equivalent sum of the CF₄ and C₂F₆ Al production emissions discussed in the previous two sections, which are
Table 7. Time averaged global C\textsubscript{2}F\textsubscript{6} emission estimates.

<table>
<thead>
<tr>
<th></th>
<th>Time averaged C\textsubscript{2}F\textsubscript{6} emissions (Gg/yr) and percentages of AGAGE emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>1.7±0.1</td>
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<tr>
<td>Harnisch et al. (1995)</td>
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<tr>
<td>Harnisch et al. (1996b)</td>
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<tr>
<td>Khalil et al. (2003)</td>
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<td>Worton et al. (2007)</td>
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<tr>
<td>EDGAR 32/FT2000</td>
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<tr>
<td>EDGAR v4 (2009)</td>
<td></td>
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<tr>
<td>IAI Anode Effect surveys (10.2% of CF\textsubscript{4} (only Al production)</td>
<td>1.0 (46%)</td>
</tr>
<tr>
<td>UNFCCC Annex I countries\textsuperscript{b}</td>
<td>1.3 (59%)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} EDGAR v4 (2009) emission estimates have been extrapolated beyond 2005 based on the 2005–2004 difference.

\textsuperscript{b} Based on PFC emission data collected by the UNFCCC process (United Nations Framework Convention on Climate Change, 2009).

based on CF\textsubscript{4} and C\textsubscript{2}F\textsubscript{6} emission factors from previous IAI Anode Effect surveys, are \textasciitilde10–15% lower until 1996 than the total CO\textsubscript{2}-e emissions directly listed in the latest IAI (2009a) survey. Afterwards the agreement is very good. If we add the (higher) CO\textsubscript{2}-e emissions listed in the latest IAI (2009a) survey to the EDGAR v4 CO\textsubscript{2}-e emissions estimated for non-metal production, the resulting sum remains significantly lower than the sum of global total AGAGE CF\textsubscript{4} and C\textsubscript{2}F\textsubscript{6} CO\textsubscript{2}-e emissions. From 1990 to 1992 the difference is \textasciitilde19 million tonnes CO\textsubscript{2}-e emissions which corresponds to \textasciitilde2.9 Gg CF\textsubscript{4} or \textasciitilde2.6 Gg CF\textsubscript{4} and \textasciitilde0.3 Gg C\textsubscript{2}F\textsubscript{6} using the C\textsubscript{2}F\textsubscript{6}/CF\textsubscript{4} emission ratio of 10.2% from Sect. 5.2. Assuming that PFC emission from China were likely small in the early 1990s this could be explained by an underestimation of CF\textsubscript{4} emissions in the IAI Anode Effect survey and/or by a significant underestimation of semiconductor/electronics manufacture emissions by EDGAR v4. Recently, the difference has grown substantially to \textasciitilde42 million tonnes of CO\textsubscript{2}-e emissions in 2005, which corresponds to \textasciitilde6.4 Gg CF\textsubscript{4}, or \textasciitilde5.6 Gg CF\textsubscript{4} and \textasciitilde0.6 Gg C\textsubscript{2}F\textsubscript{6}, similar to the CF\textsubscript{4} emission gap of \textasciitilde6.1 Gg CF\textsubscript{4} for 2005 described in Sect. 5.1, supporting the results in Sects. 5.1 and 5.2.

5.4 C\textsubscript{3}F\textsubscript{8} emissions

AGAGE global top-down C\textsubscript{3}F\textsubscript{8} emissions (Fig. 6) were \textasciitilde0.1 Gg/yr around 1975, increased to \textasciitilde0.3 Gg/yr around 1992, sharply increased to \textasciitilde1.1 Gg/yr in the mid-2000s and declined to \textasciitilde0.6 Gg/yr in 2008. Khalil et al. (2003) reported \textasciitilde50% lower average top-down emissions (Table 8). Culbertson et al. (2004) reported very similar average emissions for 1982–1987 and 1992–1997, but substantially lower emissions for 1977–1982 and 1987–1992.

Only a small fraction of C\textsubscript{3}F\textsubscript{8} emissions estimated in this work are accounted for in the EDGAR v4 emission database (2009), \textasciitilde1% in the 1970s and 1980s, \textasciitilde4–6% in the early 1990s, and \textasciitilde30% since 2003 (Fig. 6, Table 8).

The 2006–2009 emissions distribution modeled from our data is 98\%±0.4%, 1±1%, <0.2±0.2%, and <0.1±0.2% for the 30–90°N, 0–30°N, 0–30°S, and 30–90°S semi-hemispheres, respectively. EDGAR v4 estimates a similar NH:SH ratio for 2005 with 90%, 9%, 0.3%, and 1% for the same semi-hemispheres, respectively, but shifts emissions within the NH towards the tropics.

Harnisch et al. (1998) estimated primary Al production C\textsubscript{3}F\textsubscript{8} emissions of \textasciitilde0.1±0.05 Gg/yr, which are not taken into account by EDGAR v4. In the 1970s emissions from semiconductor/electronics manufacture and refrigeration/air conditioning were likely small. Assuming that the \textasciitilde0.1 Gg/yr C\textsubscript{3}F\textsubscript{8} emissions estimated here for the 1970s were related to Al production, an 1973 emissions factor of 0.0055 kg C\textsubscript{3}F\textsubscript{8}/tonne Al and a C\textsubscript{3}F\textsubscript{8}/CF\textsubscript{4} emission ratio of 0.48% (by mass) could be calculated using primary Al production data (similar to the estimation of CF\textsubscript{4} and C\textsubscript{2}F\textsubscript{6} emissions). In 2008 the 0.48% (by weight) would contribute only \textasciitilde0.02 Gg/yr, based on Al production C\textsubscript{3}F\textsubscript{8} emissions estimated from IAI Anode Effect surveys, or \textasciitilde0.05 Gg/yr if the total global CF\textsubscript{4} emissions estimated from AGAGE measurements were from Al production. Both estimates are much lower than our 0.64 Gg estimate for 2008. Either the C\textsubscript{3}F\textsubscript{8}/CF\textsubscript{4} emission ratio increased dramatically, which seems unlikely, or non-Al production C\textsubscript{3}F\textsubscript{8} sources must have gained rapid dominance. For example, C\textsubscript{3}F\textsubscript{8} has been proposed as an inert reaction medium, a dielectric, a propellant, a heat exchanger liquid, a deep-freezing agent, a refrigerant in H/F lasers, an etching agent for SiO\textsubscript{2}-coated silicon, as a component in breathing systems (von Halasz, 1978), and it is used in refrigerant mixtures (20% in R403a, 39% in R403b, 5% in R412a, 9% in R413a, 56% in R509a). Clearly, the majority of C\textsubscript{3}F\textsubscript{8} emissions are unaccounted for.
Table 8. Time averaged global C$_3$F$_8$ emission estimates.

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<tbody>
<tr>
<td>This work</td>
<td>0.12±0.01</td>
<td>0.20±0.02</td>
<td>0.26±0.03</td>
<td>0.28±0.05</td>
<td>0.65±0.06</td>
<td>1.01±0.09</td>
<td>0.76±0.05</td>
</tr>
<tr>
<td>Khalil et al. (2003)</td>
<td>0.1 (52%)</td>
<td>(1978–1986)</td>
<td>0.11 (40%)</td>
<td>0.48 (104%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDGAR 32/FT2000</td>
<td>&lt; 0.01 (0.5%)</td>
<td>&lt; 0.01 (0.5%)</td>
<td>&lt; 0.01 (0.6%)</td>
<td>0.01 (4%)</td>
<td>0.12 (18%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| EDGAR v4 (2009)           | < 0.01 (0.6%) | < 0.01 | < 0.01 | 0.01 (5%) | 0.12 (19%) | 0.28 (27%) | 0.28 (37%)$^a$
| UNFCCC Annex I countries$^b$ | 0.03 (11%) | 0.05 (7%) | 0.06 (6%) |


$^b$ Based on PFC emission data collected by the UNFCCC process (United Nations Framework Convention on Climate Change, 2009).

![Fig. 6. Global C$_3$F$_8$ emissions from the inversion of AGAGE atmospheric data with the AGAGE 2-D 12-box model compared to emissions reported by Khalil et al. (2003), Culbertson et al. (2004), the EDGAR v4 (2009) emission database, and Annex I countries (UNFCCC, 2009, Table S1). Also shown are EDGAR v4 emission estimates for refrigeration/air conditioning and semiconductor/electronics manufacture.](image)

Like CF$_4$ and C$_2$F$_6$ emissions, C$_3$F$_8$ emissions from UNFCCC data (Supplement 1, Table S1) are substantially lower than the top-down emissions based on AGAGE measurements. UNFCCC reported emissions have increased from ~0.03 Gg/yr in 1990 to ~0.06 Gg/yr in 2006, while actual emissions were ~8–32 times higher. Given the lack of knowledge about C$_3$F$_8$ emission sources and source strengths and the fact that many non-Annex I countries with significant industrial activity such as Al production and semiconductor/electronic manufacture are not included in the UNFCCC data, the discrepancy is not surprising, yet again demonstrating the need for global reporting.

Total global C$_3$F$_8$ emissions from all sources expressed as CO$_2$-e emissions add ~0.5% in the early 1970s, ~8% in 2002 and 2003, and ~5% in 2008 to the global total CF$_4$ and C$_2$F$_6$ CO$_2$-e emissions discussed in Sect. 5.3 (SAR GWP$_{100}$).

6 Summary and conclusions

We have presented measurements of the perfluorocarbons (PFCs) CF$_4$, C$_2$F$_6$, and C$_3$F$_8$ with much improved accuracies of ~1–2% on calibration scales developed for the Advanced Global Atmospheric Gases Experiment (AGAGE). The measurements have been made with the “Medusa” trace gas analytical system which achieves excellent precisions for the PFCs. We have determined long-term baseline growth rates and interhemispheric gradients in both hemispheres for CF$_4$, C$_2$F$_6$, and C$_3$F$_8$ over three decades, based on measurements of archived air and in situ real-time atmospheric measurements. We find that the abundances of CF$_4$ are ~6–10% lower than previously reported, an important finding for this long-lived and potent greenhouse gas. The pre-industrial backgrounds were measured in air extracted from Greenland ice and Antarctic firn.

Global inversions (AGAGE 2-D 12-box model) were used to estimate global CF$_4$, C$_2$F$_6$, and C$_3$F$_8$ source strength over the last three decades. The authors of the Representative Concentration Pathways (RCP) emission scenarios of the Coupled Model Intercomparison Project Phase 5 (CMIP5) for the upcoming Fifth Assessment Report (AR5) had access to our preliminary results (M. Meinshausen, personal communication, 2009). Past and present RCP CF$_4$ and C$_2$F$_6$ emissions are in reasonable agreement with AGAGE top-down emissions and future emissions are similar or drop steeply (http://www.iiasa.ac.at/web-apps/tn/RepbDb/dsd?Action=htmlpage&page=about), while many IPCC Second Assessment Report (SAR) emission scenarios started out with significantly different emissions.
and predicted very high future CF$_4$ and C$_2$F$_6$ emissions (Nakićenović et al., 2000). No C$_3$F$_8$ emission scenarios exist.

EDGAR v4 emissions and top-down emissions estimated here by AGAGE agree after ∼1990 for CF$_4$ and before ∼1992 for C$_2$F$_6$, but at other times EDGAR v4 emissions are too low. EDGAR v4 provides valuable information for atmospheric research, but being a hybrid of bottom-up methodologies and top-down estimates based on previously published atmospheric measurements, it is unclear how CF$_4$ and C$_2$F$_6$ emission components were derived and how certain they are. EDGAR v4 C$_3$F$_8$ emissions are underestimated by 100 to 200-times in the 1970s and 1980s and by 3 to 4 times since 1999. C$_3$F$_8$ emissions from Al production, not considered in EDGAR v4, can only explain a small fraction of the difference. The industrial production and usage of C$_3$F$_8$ should be investigated to find the missing emission source(s).

UNFCCC CF$_4$ and C$_2$F$_6$ emission estimates are only ∼30–70% of global AGAGE top-down emissions, since non-Annex I countries with significant Al production (i.e., China, Brazil, South Africa, India, United Arab Emirates, Bahrain) and with semiconductor/electronics manufacture (i.e., China, Taiwan) are not included in UNFCCC data to date. UNFCCC C$_3$F$_8$ emission estimates are 8–32 times lower than AGAGE top-down emissions.

The sum of CF$_4$ emissions estimated from International Aluminium Institute (IAI) Anode Effect surveys and EDGAR v4 non-metal production emissions are ∼3–5 Gg/yr too low from 1990 to 1992, and are ∼6 Gg/yr too low in 2005. Possible explanations are that IPCC methodologies as applied by IAI lead to an underestimation of Al production CF$_4$ emissions, especially from China where only a few aluminum smelters have been surveyed, and/or that semiconductor/electronics manufacture CF$_4$ emissions in EDGAR v4 are significantly underestimated, but with our current knowledge it is impossible to determine which is true. Unfortunately, the report of the World Semiconductor Council (WSC) on the voluntary perfluorocompound emissions reduction program of semiconductor manufacturers lists only relative perfluorocompound emissions and does not explain how they were measured, estimated, and/or verified. The report gives no information how the emissions of specific perfluorocarbons such as CF$_4$ or C$_2$F$_6$ have evolved and whether the use of the phrase perfluorocompounds instead of perfluorocarbons means that SF$_6$ and NF$_3$ are included in the sum, which would further complicate the interpretation of WSC data. The IAI Anode Effect surveys on PFC emissions from Al production contain many details and are based on IPCC methodology, but recent IAI reports do not list individual CF$_4$ and C$_2$F$_6$ emissions or emission factors, which also complicates the use of IAI data. Furthermore, recently Maltas et al. (2010) discovered significant PFC emissions during the startup of reduction cells which may not be accounted for by IPCC methodology. The EDGAR database does not provide all details necessary to understand how their PFC emission estimates are calculated or apportioned among source categories.

The significant discrepancies between UNFCCC, EDGAR, and IAI PFC emission estimates and global top-down emission estimates based on AGAGE measurements, the lack of details in the WSC report and the EDGAR database and possible uncertainties in IPCC methodologies, emphasize the need for more accurate, transparent, and complete global emissions reporting, and for verification with atmospheric measurements to assess the emissions of these long-lived and potent greenhouse gases. Our understanding of PFC emissions from Al production, semiconductor/electronics manufacture, and possibly other sources needs to be improved since the PFCs contribute significantly to the greenhouse gas budget of countries with large Al production (Isaksen et al., 1992) and semiconductor/electronics industries (Cook, 1995), and alter the radiative budget of the atmosphere essentially permanently. A combined effort by IAI, WSC, global PFC suppliers, and EDGAR to improve estimates of PFC emissions would be very valuable. To allow direct comparison with atmospheric observations individual CF$_4$ and C$_2$F$_6$ emissions and emission factors should be reported. High-frequency in situ CF$_4$, C$_2$F$_6$, and C$_3$F$_8$ measurements in the vicinity of important regional sources such as China, in combination with advanced 3-D modeling are needed to quantify regional emissions and to untangle the flux contributions from Al production and non-Al production sources.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/10/5145/2010/acp-10-5145-2010-supplement.pdf.

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