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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_4), hexafluoroethane (C_2F_6), and octafluoropropane (C_3F_8) in both hemispheres, measured with improved accuracies (~1–2%) and improved precisions (<0.3%, or <0.2 ppt (parts-per-trillion), for CF_4; <1.5%, or <0.06 ppt, for C_2F_6; <4.5%, or <0.02 ppt, for C_3F_8) within the Advanced Global Atmospheric Gases Experiment (AGAGE). Pre-industrial background values of 34.7±0.2 ppt CF_4 and 0.1±0.02 ppt C_2F_6 were measured in air extracted from Greenland ice and Antarctic firn. Anthropogenic sources are thought to be primary aluminum production (CF_4, C_2F_6, C_3F_8), semiconductor production (C_2F_6, CF_4, C_3F_8) and refrigeration use (C_3F_8). Global emissions calculated with the AGAGE 2-D 12-box model are significantly higher than most previous emission estimates. The sum of CF_4 and C_2F_6 emissions estimated from aluminum production and non-metal production are lower than observed global top-down emissions, with gaps of ~6.4–7.6 Gg/yr CF_4 in recent years. The significant discrepancies between previous CF_4, C_2F_6, and C_3F_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.

1 Introduction

The perfluorocarbons (PFCs) tetrafluoromethane (CF_4, PFC-14), hexafluoroethane (C_2F_6, PFC-116), and octafluoropropane (C_3F_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) 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_2F_6 and C_3F_8 have lifetimes of at least 10 000 and 2600 years and GWPs 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_2F_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_3F_8 was just recently found in the atmosphere (Culbertson et al., 2000).

CF_4, and to a smaller degree C_2F_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 lithosphere 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 with sulfur hexafluoride (SF_6). 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_2F_6 or C_3F_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_2F_6 (Worton et al., 2007).

Since the 1980s CF_4, C_2F_6, and C_3F_8 have been used increasingly in semiconductor and other electronics manufacture 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_2F_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 fluorspar 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) Aluminium Institute, 1996, 2009b). For the Southern Hemisphere (SH) a general increase in CF_4 has also been shown, but measurements were sparser and uncertainties were larger (Table 3). Corresponding stratospheric increases in CF_4 were observed (Zander et al., 1996; Zhou et al., 1998; Rinsland et al., 2006). Small C_2F_6 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 C_3F_8 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.

In the Emission Database for Global Atmospheric Research (EDGAR) v4 (2009) CF_4 and C_2F_6 emissions are mostly attributed to the production of metals (mostly Al production), followed by emissions from semiconductor/electronics manufacture, the latter gaining dominance for C_2F_6 in the mid-1990s. C_3F_8 emissions are largely attributed to refrigeration/air conditioning use and semiconductor/electronics manufacture.

For CF_4 and C_2F_6, 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, but 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_3F_8. 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 quantity emissions.

Khalil et al. (2003) addressed substantial differences in the calibration scales of up to 20% for CF_4 and 64% for C_2F_6 by multiplying their own and several other published CF_4 and C_2F_6 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 $\sim\pm10\%$ (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_4, 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% typically achieved for many halogenated trace gases (e.g., Maiss et al., 1996; Prinn et al., 2000). Clearly, more accurate PFC calibration scales and a more precise CF_4 measurement method were needed to characterize the impacts of these long-lived and potent GHGs.

Here we present measurements of CF_4, C_2F_6, and C_3F_8 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_4, C_2F_6, and C_3F_8 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 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_2F_6, and C_3F_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_2F_6, C_3F_8, and ~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_2F_6 and C_3F_8 measurements began in October 2003 at SIO, in November 2003 (C_3F_8) and January 2004 (C_2F_6) at the remote AGAGE stations Mace Head (MHD, 53° N, 10° W, Ireland), in January (C_3F_8) and April 2004 (C_2F_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_2F_6 and C_3F_8 on the SIO-2007 scale, as parts-per-trillion (ppt) dry air mole fractions. All are based on volumetric halocarbon/nitrous oxide (N_2O) mixtures via a stepwise dilution technique with large dilution factors for each step (10^3 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_2F_6 and C_3F_8 scales are based on 4 and 5 mixtures with prepared values of 4.19–4.21 ppt C_2F_6 and 2.27–2.61 ppt C_3F_8, respectively, each containing ~20 torr water vapor. The pure CF_4 (99.997%, Aldrich), C_2F_6 (99.99%, SynQuest Laboratories), C_3F_8 (>=99.9%, SynQuest Laboratories), and N_2O (99.99%, Matheson) were further purified by repeated cycles of freezing (−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 5Å, and Carboxen 1000 at −80°C (ethanol/dry ice). Each zero air sample was measured to verify insignificant halocarbon blank levels before being spiked with the halocarbon/N_2O 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_2O and halocarbon 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_2O 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_2O). Then CF_4 was released from the capillary breaker, so that it equilibrated only with the capillary breaker (~13.48 ml±0.02%) and the N_2O filled mixture canister (~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 (~0.02%). Systematic uncertainties are conservatively estimated at ~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_2F_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_3F_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_2F_6, and 0.007–0.02 ppt (1.5–4.5%) for C_3F_8 at all sites. Typical precisions for archived air samples (see next section) were ~0.08 ppt for CF_4, ~0.03 ppt for C_2F_6, ~0.01 ppt for C_3F_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_2F_6, and 0.01 ppt for C_3F_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_2F_6, and 0.006 ppt for C_3F_8. Detection limits (3 times baseline noise) for 2 L ambient air samples were ~0.2 ppt for CF_4, ~0.02 ppt for C_2F_6, and ~0.02 ppt for C_3F_8 at SIO and CSIRO.

The analytical systems showed no CF_4 blanks. At SIO small C_2F_6 and C_3F_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_2F_6 and C_3F_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_2F_6, and 0.02–0.34 ppt C_3F_8). For CF_4 and C_2F_6 no corrections were necessary, but for C_3F_8 a non-linearity correction of ~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_2F_6, and C_3F_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_2F_6 all six samples were in excellent agreement with the SH samples with similar fill dates measured at CSIRO (delta mole fraction Δx=0.01–0.16 ppt CF_4, Δx=0.02–0.03 ppt C_2F_6, Δx=0.001–0.014 ppt C_3F_8, Δt=3–33 days). For C_3F_8 one sample was rejected as an outlier with lower than expected C_3F_8 mixing ratios

(Δx=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_2F_6 three of the five samples were in excellent agreement with the NH samples with similar fill dates measured at SIO (Δx=0.07–0.13 ppt CF_4, Δx=0–0.01 ppt C_2F_6, Δt=0–9 days). For C_3F_8 four of the five samples were in excellent agreement (Δx=0–0.011 ppt C_3F_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_2F_6 mixing ratios (Δx=1.13 ppt CF_4, Δx=0.06 ppt C_2F_6, Δt=12 days). The fifth NH sample measured at CSIRO had a unique fill date (Δt=81 days to other tanks) but was rejected as a clear outlier for all PFCs. These tests show that measurements at the two sites are in agreement at least for mixing ratios ranges of 54.0–73.4 ppt CF_4, 1.2–3.4 ppt C_2F_6, and 0.06–0.37 ppt C_3F_8. Based on greater than 2σ deviations from a curve fit through all 70 (64 at CSIRO and 6 at SIO) SH samples, one CF_4, ten C_2F_6, and seven C_3F_8 samples were rejected as outliers leaving 69 CF_4 (99%), 60 C_2F_6 (86%), and 63 C_3F_8 (90%) SH samples.

The 129 unique NH samples (124 at SIO and 5 at CSIRO) were collected from several sources, mainly the laboratories of R. F. Weiss, C. D. Keeling, and R. Keeling at SIO, the Global Monitoring Division (GMD) at the National Oceanic and Atmospheric Administration (NOAA), the Norwegian Institute for Air Research (NILU), and the University of California at Berkeley (UCB). They were mostly filled during baseline conditions, but with different techniques and for different purposes. For CF_4 29 NH samples were rejected as outliers with mostly higher mixing ratios for reasons such as initial retention of analytes on drying agents used during the filling followed by breakthrough, or sampling of polluted air, leaving 100 CF_4 (76%) NH samples. Excellent atmospheric records from 1973–2007 for the NH and from 1978–2007 for the SH resulted for CF_4. For the less volatile and less abundant C_2F_6 and C_3F_8, more outliers and more scatter were observed. For C_2F_6 55 NH samples were rejected as outliers, leaving 74 C_2F_6 (57%) NH samples. For C_3F_8 56 NH samples were rejected as outliers, leaving 73 C_3F_8 (57%) NH samples. Nevertheless, consistent atmospheric records were reconstructed for C_2F_6 and C_3F_8.

2.3 Ancient air extracted from glacial ice and old air extracted from firn

To assess the pre-industrial, natural background abundances of CF_4, C_2F_6, and C_3F_8, we measured ancient NH air extracted from melted glacial ice (V. V. Petrenko and J. P. Severinghaus, SIO) which were collected in 2004 and 2005 at the Pâkitsoq site (Petrenko et al., 2008, 2009), an ice margin ablation site in Western Greenland (69.43° N, 50.25° W) (Reeh et al., 1991; Petrenko et al., 2006), where ice dating from the last glacial termination is exposed. Of the eleven samples two had ages of ∼11 360 BP (Pre-boreal), two of ∼11 550 BP (transition from Pre-Boreal to Younger Dryas), two of ∼11 600 BP (Younger Dryas), two of ∼14 500 BP (Bølling), two of ∼14 800 BP (Oldest Dryas), and one of ∼19 000 BP (Last Glacial Maximum) (BP, "before present", i.e. before 1 January 1950). We also measured old SH air extracted from Antarctic firn (J. P. Severinghaus, SIO) collected on 6–17 January 2004 in 6 L Silcosteel tanks (Restek Corp.) at the Megadunes site in Antarctica (80.78° S, 124.5° E) (Courville et al., 2007; Severinghaus et al., 2010). The deepest firn sample (67.44 m) had a mean air-age of ∼1910 based on a refined firn gas-diffusion forward model similar to Schwander et al. (1993) and Severinghaus and Battle (2006) developed at SIO (Shields et al., 2007; J. E. Shields, personal communication, 2009).

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 abundances in eight tropospheric and four stratospheric boxes, with horizontal divisions at the poles, ±30° and at the equator 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. Previous studies have shown that this 2-D model provides similar results to that of 3-D models when simulating 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 computational 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_2F_6, and C_3F_8

Annual emissions were deduced for the four semi-hemispheres using an approach based on a Bayesian discrete 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 emissions and information from each measurement, weighted by their uncertainties. Total uncertainties include those 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 sample date (1973) of air measured by AGAGE were determined using primary Al production from 1900–1972 (US Geological Survey, 1932–2009) multiplied by constant emission factors (EF, kg PFC/ton Al produced). Emissions during this period were required to spin up the model from a globally 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_2F_6 and from preliminary measurements in an Australian Al smelter for C_3F_8 and scaled throughout this model spin-up period using the 1973 emissions derived from the inversion, resulting in 1.14 kg CF_4/ton Al, 0.117 kg C_2F_6/ton Al, and 0.0055 kg C_3F_6/ton 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_4 and C_2F_6 and 20% for C_3F_8. These constraints on emission changes were included in the inversion to avoid unphysically 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, $\boldsymbol{x}$ and error covariance matrix, $\mathbf{P}$ are shown in Eqs. (1–2). $\boldsymbol{x}$ contains sub-vectors of emissions q_i for year i, with each q_i containing emissions from the four semi-hemispheres. Similarly, each element in $\mathbf{P}$ is a sub-matrix with errors from the four semi-hemispheres. The diagonal elements, σ_{ii}^2 of the error covariance matrix, contain the square of emissions errors in year 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 k and updating the emissions vector and error covariance matrix as shown by Eqs. (3–5). Superscripts f and a refer to forecasted and analyzed values, $\mathbf{H}_k$ is a Jacobian matrix describing the sensitivity of mole fractions to changes in emissions, $\boldsymbol{y}_k^0$ and $\boldsymbol{y}_k$ refer to observed and simulated mole fractions, respectively, and $\mathbf{R}_k$ is the measurement covariance matrix, with diagonal elements equal to the square of the measurement error.

$$\boldsymbol{x}_k^f = [q_1, q_2 \dots q_{37}]^T \tag{1}$$

$$\mathbf{P}_k^f = \left[\begin{array}{cc|c} \sigma_{1,1}^2 & 0 & 0 \\ 0 & \sigma_{2,2}^2 & 0 \\ \hline 0 & 0 & \sigma_{37,37}^2 \end{array}\right] \tag{2}$$

$$\boldsymbol{x}_k^a = \mathbf{K}_k(\boldsymbol{y}_k^o - \boldsymbol{y}_k) + \boldsymbol{x}_k^f \tag{3}$$

$$\mathbf{P}_k^a = (\mathbf{I} - \mathbf{K}_k\mathbf{H}_k)\mathbf{P}_k^f \tag{4}$$

$$\mathbf{K}_k = \mathbf{P}_k^f\mathbf{H}_k^T(\mathbf{H}_k\mathbf{P}_k^f\mathbf{H}_k^T + \mathbf{R}_k)^{-1} \tag{5}$$

To begin, the first measurement (at $k = 0$) 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), ± 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, instrumental precision, and scale propagation. Sampling frequency error characterizes the uncertainty that arises from using a finite number of measurements to define a

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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 is 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_4, C_2F_6, and C_3F_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 Grim Air Archive (CGAA) (Krummel et al., 2007) and background monthly mean in situ data for Cape Grim, Tasmania. 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 and Cape Meares, Oregon [NOAA/NILU samples], 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_2F_6 in the SH. For C_3F_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 and 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±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±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_2F_6 measurements

The precision of our AGAGE C_2F_6 data and the quality of the archived air measurements are improved compared to most previously reported C_2F_6 data sets, and abundances in both hemispheres are more clearly defined (Table 4 and 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_2F_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_2F_6 as a fluorine source in semiconductor/electronics manufacture in the early 1990s as indicated by the EDGAR v4 emission database (2009), followed by a gradual replacement of C_2F_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_2F_6 emissions. C_2F_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_2F_6 mixing ratios reconstructed from firn air by Worton et al. (2007) differ significantly and show different trends.

4.1.3 C_3F_8 measurements

The precision of our AGAGE C_3F_8 data is similar to the C_3F_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_2F_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_3F_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_2F_6, and C_3F_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_2F_6 firn data dated with a firn model to zero C_2F_6 abundance assuming no natural C_2F_6. This agreement is difficult to interpret, because the C_2F_6 mixing ratios at the beginning of the Worton et al. (2007) record are higher compared to AGAGE, the curvatures of the C_2F_6 abundances differ, and the CF_4 calibration scales differ significantly (Figs. 2 and 3).

We measured 0.1±0.02 ppt C_2F_6 in the lowest Megadunes firn sample. It is conceivable that this pre-industrial, background C_2F_6 level represents evidence for a small lithospheric source, as found for CF_4 by Deeds et al. (2008). C_3F_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_2F_6, and C_3F_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_2F_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. 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 supplementary Fig. S3, see http://www.atmos-chem-phys-discuss.net/10/6485/2010/acpd-10-6485-2010-supplement.pdf) 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, supplementary material and Table S1: http://www.atmos-chem-phys-discuss.net/10/6485/2010/acpd-10-6485-2010-supplement.pdf). 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. Notable non-Annex I countries that emit PFCs from Al production are China, Brazil, South Africa, India, United Arab Emirates and Bahrain, which accounted for 40% of 2006 global Al production (US Geological Survey, 1932–2009).

To validate the PFC emission reduction measures by the global aluminum industry under the auspices of the International (Primary) Aluminium Institute (IAI), IAI estimates global Al production PFC emissions using data on smelting-technology-specific Al production and PFC (CF_4 and C_2F_6) bottom-up emission factors (EF) in their IAI Anode Effect surveys (1996, 2000, 2001, 2003–2008, 2009a, b). A recent IAI survey of eight Chinese smelters using the PFPB (Point Feed Pre Bake) technology, which is used by all Chinese smelters, found an average EF 2.6 times higher than the global survey PFPB technology average previously used to estimate Chinese emissions (2009a). Global CF_4 emissions calculated from the IAI reports increase by ~0.6–1.3 Gg/yr when the increased EF for Chinese smelters is applied (supplementary material and Table S2, http://www.atmos-chem-phys-discuss.net/10/6485/2010/acpd-10-6485-2010-supplement.pdf). 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 (assuming 2005 values for 2005–2008), the resulting global sum (Fig. 4) is substantially lower than AGAGE global top-down emissions, by ~3.8 Gg/yr in the early 1990s, by ~3.1 Gg/yr in 1999, and by ~6.4 Gg/yr from 2003 to 2008.

One possible explanation is that IAI underestimates global Al production CF_4 emissions, especially from China – even after applying the 2.6 times larger PFTB EF for Chinese smelters. However, in 1990 China only produced ~4% of global Al according to IAI (2009a) and semiconductor/electronics manufacture CF_4 emissions were likely small (EDGAR v4). Therefore the observed ~3.8 Gg/yr difference in the early 1990s could indicate a small inherent underestimation of Al production CF_4 emissions calculated from the IAI surveys. In any case, the recent substantial difference of ~6.4 Gg/yr suggests that the IPCC bottom-up emission estimate methodologies likely do not give representative emission values. The IPCC process does not survey all producers, and IAI attempts to do this using IPCC methodologies. The cause of the error in estimating CF_4 emissions could fundamentally lie with the IPCC methodologies and/or with the way IAI applies them. According to 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 explanation is that the limited and uncertain information about global PFC emissions from semiconductor/electronics manufacture in EDGAR v4, including from China, may lead to significantly underestimated CF_4 emissions from this source. However, 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 fluorine sources such as NF_3 (Air Products, personal communication, 2009) which should slowly reduce CF_4 emissions from semiconductor/electronics manufacture, in agreement with EDGAR v4. It is also difficult to understand why Annex I UNFCCC CF_4 emissions (Al and non-Al production) agree so well with global Al production related CF_4 emissions estimated from the IAI reports which use the same IPCC methodology, when a large fraction of Al is produced in non-Annex I countries.

5.2 C_2F_6 emissions

AGAGE global top-down C_2F_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_2F_6 emissions (Fig. 5) as expected from their lower reconstructed C_2F_6 rise rate (Fig. 2).

While C_2F_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, C_2F_6 emissions after 1991 are lower in EDGAR v4 by ~0.5 Gg/yr. It is unclear why EDGAR v4 C_2F_6 emissions agree with AGAGE results before ~1992, while CF_4 emissions only agree after ~1990, especially as C_2F_6 emissions are often estimated as a constant fraction of CF_4 emissions. As is the case for CF_4, EDGAR v4 C_2F_6 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 CF_4 emissions, estimated C_2F_6 emissions from UNFCCC data (supplementary material, Table S1, http://www.atmos-chem-phys-discuss.net/10/6485/2010/acpd-10-6485-2010-supplement.pdf) are substantially lower than emissions based on AGAGE measurements. UNFCCC reported Annex I country emissions have declined about a factor of two 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.

Smelter technology-specific Al production emission ratios of C_2F_6/CF_4 (by mass) for 1990 and 2000 reported by IAI (2001, 2003) are similar and industrial average emission ratios were ~10% C_2F_6/CF_4 (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 CF_4 and C_2F_6 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% C_2F_6/CF_4 (by mass) from Al production. Lacking further information, we estimate later Al production C_2F_6 emissions by multiplying the Al production CF_4 emissions from the IAI Anode Effect surveys (Sect. 5.1) by this emission ratio. Resulting Al production C_2F_6 emissions (Fig. 5) are lower than or similar to EDGAR v4 emissions from metal production (mostly Al). When EDGAR v4 non-metal production C_2F_6 emissions (>97% from semiconductor/electronics manufacture) are added to our Al production C_2F_6 emission estimates, the sums are lower than our global AGAGE top-down emission estimates.

If the differences between global top-down AGAGE CF_4 emissions and the sums of Al production CF_4 emissions (IAI Anode Effect survey) and non-Al production emissions (EDGAR v4) are due to underestimated Al production CF_4 emissions, the estimate for Al production C_2F_6 emissions would need to be increased correspondingly by 10.2% (by mass) of the CF_4 difference. The resulting sum of Al and non-Al production C_2F_6 emissions would agree much better with AGAGE emissions from 2002–2005 (difference ∼0.2 Gg/yr), but emissions from 1990–2001 would remain underestimated by ∼0.4 Gg/yr, either because the assumptions are wrong or because EDGAR v4 semiconductor/electronics manufacture C_2F_6 emissions from 1990–2001 are also underestimated.

5.3 CF_4 and C_2F_6 equivalent CO_2 emissions

Recent IAI Anode Effect surveys report a sum of total CF_4 and C_2F_6 CO_2-equivalent (CO_2-e) emissions using IPCC 2001 Second Assessment Report (SAR) global warming potentials (100-yr GWPs, Table 1) rather than separate CF_4 and C_2F_6 emissions or emission factors. Since the 2006 IAI Anode Effect survey (2008) total CO_2-e emissions reported for 1990 and 1995 are ∼10% higher than in previous surveys, probably due to the change from IPCC 2000 to IPCC 2006 methodology, but CO_2-e emissions reported for 2000, 2004, and 2005 remain very similar. Correspondingly the CO_2-equivalent sum of the CF_4 and C_2F_6 Al production emissions discussed in the previous two sections, which are based on CF_4 and C_2F_6 emission factors from previous IAI Anode Effect surveys, are ∼10% lower until 1996 than the total CO_2-e emissions directly listed in the latest IAI (2009a) survey. Afterwards the agreement is very good. If we add the (higher) CO_2-e emissions listed in the latest IAI (2009a) survey to the EDGAR v4 CO_2-e emissions estimated for non-metal production (extrapolated after 2005 based on the 2005–2004 difference), the resulting sum remains significantly lower than the sum of global total AGAGE CF_4 and C_2F_6 CO_2-e emissions. In the early 1990s the difference of ∼20 million tonnes CO_2-e emissions corresponds to ∼3.1 Gg CF_4 or ∼2.7 Gg CF_4 and ∼0.3 Gg C_2F_6 using the C_2F_6/CF_4 emission ratio of 10.2% from Sect. 5.2. Taking the uncertainties of the inversion into account, this indicates an inherent underestimation of CF_4 emissions by the IAI Anode Effect surveys as found in Sect. 5.2. Recently, the difference is substantially larger, ∼49 million tons of CO_2-e emissions, corresponding to ∼7.6 Gg CF_4, or ∼6.6 Gg CF_4 and ∼0.7 Gg C_2F_6, similar to the CF_4 emission gap of ∼6.4 Gg CF_4 found in Sect. 5.1, supporting the results in Sects. 5.1 and 5.2.

5.4 C_3F_8 emissions

AGAGE global top-down C_3F_8 emissions (Fig. 6) were ∼0.1 Gg/yr around 1975, increased to ∼0.3 Gg/yr around 1992, sharply increased to ∼1.1 Gg/yr in the mid-2000s and declined to ∼0.6 Gg/yr in 2008. Khalil et al. (2003) reported ∼50% 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_3F_8 emissions estimated in this work are accounted for in the EDGAR v4 emission database (2009), <1% in the 1970s and 1980s, ∼4–6 % in the early 1990s, and ∼30% since 2003 (Fig. 6, Table 8).

The 2006–2009 emissions distribution modeled from our data is 98±0.4%, 1±1%, <0.1±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_3F_8 emissions of ~0.1±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 ~0.1 Gg/yr C_3F_8 emissions estimated here for the 1970s were related to Al production, an 1973 emissions factor of 0.0055 kg C_3F_8/ton Al and a C_3F_8/CF_4 emission ratio of 0.48% (by mass) could be calculated using primary Al production data (similar to CF_4 and C_2F_6 emissions). In 2008 this emission ratio would contribute only ~0.05 Gg/yr, based on Al production CF_4 emissions estimated from IAI Anode Effect surveys. Either the C_3F_8/CF_4 emission ratio increased dramatically, which seems unlikely, or other C_3F_8 sources must have gained rapid importance. For example, C_3F_8 has been proposed as an inert reaction medium, a dielectric, a propellant, a heat exchanger liquid, a deep-freezing agent, a fluorine component in H/F lasers, an etching agent for SiO_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_3F_8 emissions are unaccounted for.

Like CF_4 and C_2F_6 emissions, C_3F_8 emissions from UNFCCC data (supplementary material, Table S1, see http://www.atmos-chem-phys-discuss.net/10/6485/2010/acpd-10-6485-2010-supplement.pdf) 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_3F_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.

C_3F_8 emissions add ~8% to the CF_4 and C_2F_6 CO_2-e emissions in Sect. 5.3 (SAR GWPs).

6 Summary and conclusions

We have presented measurements of the perfluorocarbons (PFCs) CF_4, C_2F_6, and C_3F_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_2F_6, and C_3F_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_2F_6, and C_3F_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_2F_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/tnt/RcpDb/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_2F_6 emissions (Nakićenović et al., 2000). No C_3F_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_2F_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_2F_6 emission components were derived and how certain they are. EDGAR v4 C_3F_8 emissions are underestimated by 100 to 200-times in the 1970s and 1980s and by 3 to 4 times since 1999. 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_3F_8 should be investigated to find the missing emission source(s).

UNFCCC CF_4 and C_2F_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, South Korea, Taiwan) are not included in UNFCCC data to date. UNFCCC C_3F_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 Survey reports and EDGAR v4 non-metal production emissions are ~2.7–3.8 Gg/yr too low in the early 1990s, and are ~6.4–7.6 Gg/yr too low in recent years. Possible explanations are that IPCC methodologies as applied by IAI lead to an underestimation of Al production CF_4 emissions, or that semiconductor/electronics manufacture CF_4 emissions in EDGAR v4 are underestimated, but with our current knowledge it is impossible to determine which is true.

The significant discrepancies between UNFCCC, EDGAR, and IAI PFC emission estimates and global top-down emission estimates based on AGAGE measurements emphasize the need for more accurate, transparent, and complete emission 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, semi-conductor/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. High-frequency in situ CF_4, C_2F_6, and C_3F_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.

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References

Abrahamson, D.: Aluminium and global warming, Nature, 356, p. 484, doi:10.1038/356484a0, 1992.

Aoki, N. and Makide, Y.: Precise determination of the atmospheric CF_4 concentration by using natural Kr in the atmosphere as an internal reference in the preconcentration/GC/MS analysis, Chem. Lett., 33, 1634–1635, 2004.

Aoki, N. and Makide, Y.: The concentration of krypton in the atmosphere - Its revision after half a century, Chem. Lett., 34, 1396–1397, 2005.

Cicerone, R. J.: Atmospheric Carbon Tetrafluoride – Nearly Inert-Gas, Science, 206, 59–61, 1979.

Clerbaux, C., Cunnold, D. M., Anderson, J., Engel, A., Fraser, P. J., Mahieu, E., Manning, A., Miller, J., Montzka, S. A., Nassar, R., Prinn, R., Reimann, S., Rinsland, C. P., Simmonds, P., Verdonik, D., Weiss, R., Wuebbles, D., and Yokouchi, Y.: Long-Lived Compounds, Chapter 1, in: Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project-Report No. 50, 572 pp., World Meteorological Organization, Geneva, Switzerland, 2007.

Cook, E.: Lifetime Commitments: Why climate policy-makers can't afford to overlook fully fluorinated compounds, World Resource Institute, Washington, USA, 2, 1995.

Courville, Z. R., Albert, M. R., Fahnestock, M. A., Cathles, L. M., and Shuman, C. A.: Impacts of an accumulation hiatus on the physical properties of firn at a low-accumulation polar site, J. Geophys. Res., 112, F02030, doi:02010.01029/02005JF000429, 2007.

Culbertson, J. A., Prins, J. M., and Grimsrud, E. P.: Improvements in the detection and analysis of CF_3-containing compounds in the background atmosphere by gas chromatography-high-resolution mass spectrometry, J. Chromatogr., 903, 261–265, 2000.

Culbertson, J. A., Prins, J. M., Grimsrud, E. P., Rasmussen, R. A., Khalil, M. A. K., and Shearer, M. J.: Observed trends for CF_3-containing compounds in background air at Cape Meares, Oregon, Point Barrow, Alaska, and Palmer Station, Antarctica, Chemosphere, 55, 1109–1119, 2004.

Cunnold, D. M., Prinn, R. G., Rasmussen, R. A., Simmonds, P. G., Alyea, F. N., Cardelino, C. A., Crawford, A. J., Fraser, P. J., and Rosen, R. D.: The Atmospheric Lifetime Experiment, 3. Lifetime Methodology and Application to 3 Years of $CFCl_3$ Data, J. Geophys. Res., 88, 8379–8400, 1983.

Cunnold, D. M., Fraser, P. J., Weiss, R. F., Prinn, R. G., Simmonds, P. G., Miller, B. R., Alyea, F. N., and Crawford, A. J.: Global Trends and Annual Releases of CCl_3F and CCl_2F_2 Estimated from ALE/GAGE and Other Measurements from July 1978 to June 1991, J. Geophys. Res., 99, 1107–1126, 1994.

Cunnold, D. M., Steele, L. P., Fraser, P. J., Simmonds, P. G., Prinn, R. G., Weiss, R. F., Porter, L. W., O'Doherty, S., Langenfelds, R. L., Krummel, P. B., Wang, H. J., Emmons, L., Tie, X. X., and Dlugokencky, E. J.: In situ measurements of atmospheric methane at GAGE/AGAGE sites 1985–2000 and resulting source inferences, J. Geophys. Res., 107(D14), 4225 doi:10.1029/2001JD001226, 2002.

Deeds, D. A., Vollmer, M. K., Kulongoski, J. T., Miller, B. R., Mühle, J., Harth, C. M., Izbicki, J. A., Hilton, D. R., and Weiss, R. F.: Evidence for crustal degassing of CF_4 and SF_6 in Mojave

Desert groundwaters, Geochim. Cosmochim. Acta, 72, 999–1013, 2008.

EDGAR: European Commission, Joint Research Centre (JRC)/Netherlands Environmental Assessment Agency (PBL). Emission Database for Global Atmospheric Research (EDGAR), release version 4.0., online available at: http://edgar.jrc.ec.europa.eu, 2009.

Fabian, P., Borchers, R., Penkett, S. A., and Prosser, N. J. D.: Halocarbons in the stratosphere, Nature, 294, 733–735, 1981.

Fabian, P., Borchers, R., Kruger, B. C., and Lal, S.: CF_4 and C_2F_6 in the Atmosphere, J. Geophys. Res., 92, 9831–9835, 1987.

Fabian, P., Borchers, R., Leifer, R., Subbaraya, B. H., Lal, S., and Boy, M.: Global stratospheric distribution of halocarbons, Atmos. Environ., 30, 1787–1796, 1996.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Dorland, R. V.: Changes in Atmospheric Constituents and in Radiative Forcing, in: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., M.Tignor, and Miller, H. L., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2007.

Gassmann, M.: Freon-14 in Pure Krypton and in Atmosphere, Naturwissenschaften, 61, 127–127, 1974.

Goldman, A., Murcray, D. G., Murcray, F. J., Cook, G. R., Vanallen, J. W., Bonomo, F. S., and Blatherwick, R. D.: Identification of the V3-Vibration-Rotation Band of CF_4 in Balloon-Borne Infrared Solar Spectra, Geophys. Res. Lett., 6, 609–612, 1979.

Harnisch, J., Borchers, R., and Fabian, P.: Estimation of tropospheric trends (1980-1995) for CF_4 and C_2F_6 from stratospheric data, Proc. SPIE, 2506, 384–393, doi:10.1117/12.221039, 1995.

Harnisch, J., Borchers, R., Fabian, P., Gaggeler, H. W., and Schotterer, U.: Effect of natural tetrafluoromethane, Nature, 384, p. 32, 1996a.

Harnisch, J., Borchers, R., Fabian, P., and Maiss, M.: Tropospheric trends for CF_4 and C_2F_6 since 1982 derived from SF_6 dated stratospheric air, Geophys. Res. Lett., 23, 1099–1102, 1996b.

Harnisch, J. and Eisenhauer, A.: Natural CF_4 and SF_6 on Earth, Geophys. Res. Lett., 25, 2401–2404, 1998.

Harnisch, J., Wing, I. S., Jacoby, H. D., and Prinn, R. G.: Primary Aluminum Production: Climate Policy, Emissions and Costs, Massachusetts Institute of Technology, Report #44, 1998.

Harnisch, J., Borchers, R., Fabian, P., and Maiss, M.: CF_4 and the age of mesospheric and polar vortex air, Geophys. Res. Lett., 26, 295–298, 1999.

Harnisch, J.: Atmospheric perfluorocarbons: sources and concentrations, in: Non-CO_2 greenhouse gases: scientific understanding, control and implementation, edited by: van Ham, J., Baede, A., Meyer, L., and Ybema, R., Kluwer Academic Publishers, Netherlands, 205–210, 2000.

Harnisch, J., Frische, M., Borchers, R., Eisenhauer, A., and Jordan, A.: Natural fluorinated organics in fluorite and rocks, Geophys. Res. Lett., 27, 1883–1886, 2000.

Harnisch, J., Agyemang-Bonsu, W. K., Katima, J. H. Y., Rosland, A., Marks, J., Born, M. F., Green, L., Kvande, H., Martchek, K., and Rand, S.: Volume 3, Industrial Processes and Product Use, Chapter 4.4, Metal Industry Emissions, Primary aluminium production, in: 2006 IPCC Guidelines for National Greenhouse Gas Inventories, IGES, Hayama, Japan, 2006.

Holliday, R. D. and Henry, J. L.: Anode Polarization Fluorocarbon Formation in Aluminum Reduction Cells, J. Ind. Eng. Chem., 51, 1289–1292, 1959.

Hurley, M. D., Wallington, T. J., Buchanan, G. A., Gohar, L. K., Marston, G., and Shine, K. P.: IR spectrum and radiative forcing of CF_4 revisited, J. Geophys. Res., 110, D02102, doi:10.1029/2004JD005201, 2005.

International Aluminium Institute: Anode effect survey 1994–1997 and Perfluorocarbon Compounds Emissions Survey 1990–1997, International Aluminium Institute, London, 2000.

International Aluminium Institute: Perfluorocarbon Emissions Reduction Programme 1990-2000, International Aluminium Institute, London, 2001.

International Aluminium Institute: The International Aluminium Institute('s) Report on the Aluminium Industry's Global Perfluorocarbon Gas Emissions Reduction Programme – Results of the 2001–2006 Anode Effect Survey, International Aluminium Institute, London, 2003–2008.

International Aluminium Institute: The International Aluminium Institute Report on the Aluminium Industry's Global Perfluorocarbon Gas Emissions Reduction Programme – Results of the 2008 Anode Effect Survey, International Aluminium Institute, London, 2009a.

International Aluminium Institute: The International Aluminium Institute Report on the Aluminium Industrys Global Perfuorocarbon Gas Emissions Reduction Programme – Results of the 2007 Anode Effect Survey, International Aluminium Institute, London, 2009b.

International Primary Aluminium Institute: Anode effect and PFC emission survey 1990–1993, International Primary Aluminium Institute, London, 1996.

Isaksen, I. S. A., Brühl, C., Molina, M., Schiff, H., Shine, K., and Stordal, F.: An assessment of the role of CF_4 and C_2F_6 as greenhouse gases, Center for International Climate and Environmental Research, Oslo, Policy Note 1992:6, 1992.

Jain, A. K., Briegleb, B. P., Minschwaner, K., and Wuebbles, D. J.: Radiative forcings and global warming potentials of 39 greenhouse gases, J. Geophys. Res., 105, 20773–20790, 2000.

Khalil, M. A. K. and Rasmussen, R. A.: Atmospheric Carbontetrafluoride (CF_4): Sources and Trends, Geophys. Res. Lett., 12, 671–672, 1985.

Khalil, M. A. K., Rasmussen, R. A., Culbertson, J. A., Prins, J. M., Grimsrud, E. P., and Shearer, M. J.: Atmospheric perfluorocarbons, Environ. Sci. Technol., 37, 4358–4361, 2003.

Kranz, R.: Organische Fluor-Verbindungen in den Gaseinschlussen der Wolsendorfer Flussspate, Naturwissenschaften, 53, 593–600, 1966.

Krummel, P. B., Langenfelds, R., Fraser, P. J., Steele, L. P., and Porter, L. W.: Archiving of Cape Grim air, in: Baseline Atmospheric Program Australia 2005–2006, edited by: Cainey, J. M., Derek, N., and Krummel, P. B., Australian Bureau of Meteorology and CSIRO Marine and Atmospheric Research, Melbourne, Australia, 55–57, 2007.

Lide, D. R.: CRC Handbook of Chemistry and Physics, 1993–1994, 74 th ed., CRC Press Inc., Boca Raton, USA, 1993.

Lide, D. R.: CRC Handbook of Chemistry and Physics, 2003–2004, CRC Press Inc., Boca Raton, USA, 2003.

Maiss, M., Steele, L. P., Francey, R. J., Fraser, P. J., Langenfelds, R. L., Trivett, N. B. A., and Levin, I.: Sulfur hexafluoride - A powerful new atmospheric tracer, Atmos. Environ., 30, 1621–1629, 1996.

Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Greally, B. R., Mühle, J., and Simmonds, P.: Medusa: A Sample Preconcentration and GC/MS Detector System for in Situ Measurements of Atmospheric Trace Halocarbons, Hydrocarbons, and Sulfur Compounds, Anal. Chem., 80, 701536–701545, doi:10.1021/ac702084k, 2008.

Morris, R. A., Miller, T. M., Viggiano, A. A., Paulson, J. F., Solomon, S., and Reid, G.: Effects of electron and ion reactions on atmospheric lifetimes of fully fluorinated compounds, J. Geophys. Res., 100, 1287–1294, 1995.

Nakićenović, N., Alcamo, J., Davis, G., de Vries, B., Fenhann, J., Gaffin, S., Gregory, K., Grübler, A., Jung, T. Y., Kram, T., La Rovere, E. L., Michaelis, L., Mori, S., Morita, T., Pepper, W., Pitcher, H., Price, L., Raihi, K., Roehrl, A., Rogner, H.-H., Sankovski, A., Schlesinger, M., Shukla, P., Smith, S., Swart, R., van Rooijen, S., Victor, N., and Dad, Z.: IPCC Special

Report on Emissions Scenarios, 599, 2000.

Olivier, J. G. J. and Berdowski, J. J. M.: Global emissions sources and sinks, in: The Climate System, edited by: Berdowski, J., Guicherit, R., and Heij, B. J., A.A. Balkema Publishers/Swets & Zeitlinger Publishers, Lisse, The Netherlands, 33–78, 2001.

Penkett, S. A., Prosser, N. J. D., Rasmussen, R. A., and Khalil, M. A. K.: Atmospheric Measurements of CF_4 and Other Fluorocarbons Containing the CF_3 Grouping, J. Geophys. Res., 86, 5172–5178, 1981.

Petrenko, V. V., Severinghaus, J. P., Brook, E. J., Reeh, N., and Schaefer, H.: Gas records from the West Greenland ice margin covering the Last Glacial Termination: a horizontal ice core, Quaternary Sci. Rev., 25, 865–875, 2006.

Petrenko, V. V., Severinghaus, J. P., Brook, E. J., Mühle, J., Headly, M., Harth, C. M., Schaefer, H., Reeh, N., Weiss, R. F., Lowe, D., and Smith, A. M.: A novel method for obtaining very large ancient air samples from ablating glacial ice for analyses of methane radiocarbon, J. Glaciol., 54, 233–244, 2008.

Petrenko, V. V., Smith, A. M., Brook, E. J., Lowe, D., Riedel, K., Brailsford, G., Hua, Q., Schaefer, H., Reeh, N., Weiss, R. F., Etheridge, D., and Severinghaus, J. P.: $^{14}CH_4$ Measurements in Greenland Ice: Investigating Last Glacial Termination CH_4 Sources, Science, 324, 1168506–1168508, doi:10.1126/science.1168909, 2009.

Prinn, R. G.: Measurement equation for trace chemicals in fluids and solution of its inverse, in: Inverse Methods in Global Biogeochemical Cycles, Geophys. Monogr. Ser., edited by: Kasibhatla, P., Heimann, M., Rayner, P., Mahowald, N., Prinn, R. G., and Hartley, D. E., American Geophysical Union, Washington, DC, 3–18, 2000.

Prinn, R. G., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Cunnold, D. M., Alyea, F. N., O'Doherty, S., Salameh, P., Miller, B. R., Huang, J., Wang, R. H. J., Hartley, D. E., Harth, C., Steele, L. P., Sturrock, G., Midgley, P. M., and McCulloch, A.: A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, J. Geophys. Res., 105, 17751–17792, 2000.

Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G., McCulloch, A., Harth, C., Salameh, P., O'Doherty, S., Wang, R. H. J., Porter, L., and Miller, B. R.: Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades, Science, 292, 1882–1888, 2001.

Rasmussen, R. A., Penkett, S. A., and Prosser, N.: Measurement of Carbon Tetrafluoride in the Atmosphere, Nature, 277, 549–551, 1979.

Ravishankara, A. R., Solomon, S., Turnipseed, A. A., and Warren, R. F.: Atmospheric lifetimes of long-lived halogenated species, Science, 259, 194–199, 1993.

Reeh, N., Oerter, H., Letreguilly, A., Miller, H., and Hubberten, H. W.: A New, Detailed Ice-Age Oxygen-18 Record from the Ice-Sheet Margin in Central West Greenland, Global Planet. Change, 90, 373–383, 1991.

Rinsland, C. P., Mahieu, E., Zander, R., Nassar, R., Bernath, P., Boone, C., and Chiou, L. S.: Long-term stratospheric carbon tetrafluoride (CF_4) increase inferred from 1985–2004 infrared space-based solar occultation measurements, Geophys. Res. Lett., 33, L02808, doi:02810.01029/02005GL024709, 2006.

Schwander, J., Barnola, J. M., Andrie, C., Leuenberger, M., Ludin, A., Raynaud, D., and Stauffer, B.: The Age of the Air in the Firn and the Ice at Summit, Greenland, J. Geophys. Res., 98, 2831–2838, 1993.

Severinghaus, J. P. and Battle, M. O.: Fractionation of gases in polar ice during bubble close-off: New constraints from firn air Ne, Kr and Xe observations, Earth Planet. Sci. Lett., 244, 474–500, 2006.

Severinghaus, J. P., Albert, M. R., Courville, Z., Fahnestock, M., Kawamura, K., Montzka, S., Mühle, J., Scambos, T., Shields, E., Shuman, C., Suwa, M., Tans, P., and Weiss, R. F.: Deep air convection in the firn at a zero-accumulation site, central Antarctica, Earth Planet. Sci. Lett., in in press, 2010.

Shields, J. E., Mühle, J., Severinghaus, J. P., and Weiss, R. F.: Reconstructing Atmospheric Histories of Halogenated Compounds to Preindustrial Times Using Antarctic Firn Air, Eos Trans. AGU, 88, Fall Meet. Suppl., Abstract A44B-06, 2007.

Symonds, R. B., Rose, W. I., and Reed, M. H.: Contribution of Cl- and F-bearing gases to the atmosphere by volcanos, Nature, 334, 415–418, 1988.

Taberaux, A. T.: Anode Effects, PFCs, Global Warming, and the Aluminum-Industry, J. Miner. Met. Mater. Soc., 46, 30–34, 1994.

Tsai, W.-T., Chen, H.-P., and Hsien, W.-Y.: A review of uses, environmental hazards and recovery/recycle technologies of perfluorocarbons (PFCs) emissions from the semiconductor manufacturing processes, J. Loss Prev. Process Ind., 15, 65–75, 2002.

US Geological Survey: Minerals Yearbook, edited by: Plunkert, P. A. and Bray, E. L., US Geological Survey, Washington, DC, 1932–2009, online available at: http://minerals.usgs.gov/minerals/pubs/commodity/aluminum/, 2010 .

United Nations Framework Convention on Climate Change: online available at: http://unfccc.int/

national_reports/annex_i_ghg_inventories/national_inventories_submissions/items/4771.php, 2009.

Victor, D. G. and MacDonald, G. J.: A model for estimating future emissions of sulfur hexafluoride and perfluorocarbons, Climatic Change, 42, 633–662, 1999.

von Halasz, S. P.: Process for the manufacture of octafluoropropane, US Patent 4,158,023, 1978.

Weiss, R. F., Mühle, J., Salameh, P. K., and Harth, C. M.: Nitrogen trifluoride in the global atmosphere, Geophys. Res. Lett., 35, L20821, doi:20810.21029/22008GL035913, 2008.

Worton, D. R., Sturges, W. T., Gohar, L. K., Shine, K. P., Martinerie, P., Oram, D. E., Humphrey, S. P., Begley, P., Gunn, L., Barnola, J.-M., Schwander, J., and Mulvaney, R.: Atmospheric Trends and Radiative Forcings of CF_4 and C_2F_6 Inferred from Firn Air, Environ. Sci. Technol., 41, 2184–2189, doi:2110.1021/es061710t, 2007.

Zander, R., Solomon, S., Mahieu, E., Goldman, A., Rinsland, C. P., Gunson, M. R., Abrams, M. C., Chang, A. Y., Salawitch, R. J., Michelsen, H. A., Newchurch, M. J., and Stiller, G. P.: Increase of stratospheric carbon tetrafluoride (CF_4) based on ATMOS observations from space, Geophys. Res. Lett., 23, 2353–2356, 1996.

Zhihong, W., Seidel, S., Atkinson, M., and Agyemang-Bonsu, W.: Chapter 3.3, Industrial Processes, PFC Emissions from Aluminium Production, in: IPCC Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories, IGES, Hayama, Japan, 2001.

Zhou, D. K., Bingham, G. E., Anderson, G. P., and Nadile, R. M.: CIRRIS-1A measurements of stratospheric carbon tetrachloride (CCl_4) and carbon tetrafluoride (CF_4), Geophys. Res. Lett., 25, 325–328, 1998.

Table 1. Lifetimes and global warming potentials of CF_4, C_2F_6, and C_3F_8.

		Lifetime	Global Warming Potential (GWP)		
Formula	Name	years	100-yr horizon (SAR[a])	100-yr horizon (AR4[b])	500-year horizon (AR4)
CF_4	PFC-14	50 000	6500	7390	11 200
C_2F_6	PFC-116	10 000	9200	12 200	18 200
C_3F_8	PFC-218	2600	7000	8830	12 500

[a] IPCC Second Assessment Report. [b] IPCC Fourth Assessment Report.

Table 2. Estimates of natural portions of accumulated atmospheric CF_4, C_2F_6, and C_3F_8.

	CF_4 (ppt)	C_2F_6 (ppt)	C_3F_8 (ppt)
This work	34.66±0.16 (Greenland)[a]		
This work	34.90±0.04 (Antarctica)[a]		
This work	34.7±0.2 (overall average)[a]	0.1±0.02	<0.02 (not detected)
Worton et al. (2007)	34±1	<0.3	
Khalil et al. (2003)	40, 43.8	all anthropogenic	all anthropogenic
Harnisch et al. (1996b)	~ 44	all anthropogenic	
Harnisch et al. (1996a)[b]	39±6		
Fabian et al. (1987)[b]	~ 43.5	all anthropogenic	

[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 SF_6 dated stratospheric air.

Table 3. CF_4 measurement precisions, scale accuracies, sample origins, and tropospheric trends.

	precision	accuracy, scale	sample origin	NH rise rate (ppt/yr)		SH rise rate (ppt/yr)	
This work	0.06–0.3%,	~1–2% , SIO-2005	troposphere	1973–1991	1.080±0.007	1978–1992	1.067±0.013
This work	0.05–0.2 ppt		troposphere	1993–2008	0.686±0.002	1994–2008	0.702±0.001
Khalil and Rasmussen (1985)	–	–	troposphere	–	–	1978–1984	0.8–2
Harnisch et al. (1995)	±5%[b]	±10%, MPAE 86[b]	stratosphere[a]	1978–1994	0.97±0.07[a]	[a]	same as NH[a]
Harnisch et al. (1996b)	±5%[b]	±10%, MPAE 86[b]	stratosphere[a]	1982–1995	1.00±0.05[a]	[a]	same as NH[a]
Harnisch et al. (1999)	~ ±2.4 ppt[b]	MPAE 86[b]	troposphere	1978–1990	1.07±0.14	–	–
Harnisch et al. (1999)			troposphere	1992–1998	0.72±0.11	–	–
Khalil et al. (2003)[c]	±1 ppt	±10%, MPAE 86[e]	troposphere	1978–1986	1.1±0.2	–	–
Khalil et al. (2003)[c]			troposphere	1986–1997	0.85±0.15	1994–1997	0.29±0.31[c]
Worton et al. (2007)	~ 1 – 2 ppt	±10 ppt, ±13.9%, UEA	firn	1955–2003	~ 0.8[d]	1955–2003	~ 0.8[d]

[a] Global tropospheric trend inferred from SF_6 dated stratospheric air.

[b] Fabian et al. (1987) reported precisions of 5–15% and accuracies of ±10% for MPAE 86. Harnisch and Eisenhauer (1998) reported accuracies of <5%.

[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 CF_4 measurements based on $CF_4/^{80}Kr$ ratios, but the method is complicated due to uncertainties in the tropospheric ^{80}Kr abundance (see Section 4.1.1).

Table 4. C_2F_6 measurement precisions, scale accuracies, sample origins, and tropospheric trends.

	precision	accuracy, scale	sample origin	NH rise rate (ppt/yr)		SH rise rate (ppt/yr)	
This work	0.5–1.5%, 0.02–0.06 ppt	∼1–2%, SIO-2007	troposphere	1973–1996,	∼0.084	1978–1997	∼0.087±0.001
This work			troposphere	1998–2004,	∼0.118	1998–2004	∼0.119±0.001
This work			troposphere	2004–2008,	∼0.900	2005–2008	∼0.099±0.002
Harnisch et al. (1995)	±10%[b]	±10%[b], MPAE 86	stratosphere[a]	1980–1995	0.086±0.005[a]	[a]	[a]
Harnisch et al. (1996b)	±10%[b]	±10%[b], MPAE 86	stratosphere[a]	1982–1995	0.084±0.005[a]	[a]	[a]
Khalil et al. (2003)	∼ ±0.05 ppt	±10%[c], MPAE 86[d]	troposphere	1978–1986	0.07±0.01	–	–
Khalil et al. (2003)			troposphere	1987–1997	0.09±0.015	1994–1997	0.072±0.019[d]
Worton et al. (2007)	±0.4–2 ppt	±10%, UEA	firn	1940–2003	∼factor 10[e]	1940–2003	∼factor 10[e]

[a] Tropospheric trend inferred from SF_6 dated stratospheric air.

[b] Fabian et al. (1981; 1987) reported precisions of ±10–15% and accuracies of ±10% (MPAE 86) for stratospheric measurements.

[c] See also Culbertson et al. (2000).

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

[e] Worton et al. (2007) state an increase by a factor of ∼10 (from 0.3 to 2.9 ppt) with a gradually increasing trend.

Table 5. C_3F_8 measurement precisions, scale accuracies, sample origins, and tropospheric trends.

	precisions	accuracies, scale	sample origin	NH rise rate (ppt/yr)		SH rise rate (ppt/yr)	
This work	1.5–4.5%, 0.007–0.020 ppt	∼1–2%, SIO-2007	troposphere	1973–1989	0.0062±0.0004	1978–1995	0.0066±0.0002
This work			troposphere	1996–2000	0.024±0.002	1996–2001	0.024±0.001
This work			troposphere	2003–2007	0.023±0.001	2001–2004	0.033±0.003
This work			troposphere	2007–2008	0.015±0.001	2004–2008	0.024±0.002
Khalil et al. (2003)	0.007 ppt	±10%[b]	troposphere	1978–1986	0.0034±0.0011		
Khalil et al. (2003)			troposphere	1987–1997	0.009±0.002	1994–1997	0.014±0.003[a]
Culbertson et al. (2004)	0.014 ppt	±10%	troposphere	1978–1998	increasing		
Culbertson et al. (2004)			troposphere	1986–1998	∼0.012	1992–1998	∼0.012

[a] SH trend based on an error weighted linear fit of the Khalil et al. (2003) data.

[b] See also Culbertson et al. (2000).

Table 6. Time averaged global CF_4 emission estimates.

	Time averaged CF_4 emissions (Gg/yr) and percentages of AGAGE emissions						
	1975–1979	1980–1984	1985–1989	1990–1994	1995–1999	2000–2004	2005–2008
This work	16.6±0.5	17.7±0.7	15.8±0.7	13.6±0.7	11.1±0.6	10.9±0.6	10.5±0.4
Harnisch et al. (1995)		14 (89%) (1978–1995)					
Harnisch et al. (1996b)		14.6 (99%) (1982–1996)					
Harnisch et al. (1999)		16.3 (96%) (1978–1990)		11.0 (94%) (1992–1998)			
Khalil et al. (2003)	14.2 (86%)	15.7 (88%)	15.4 (98%)	10.7 (79%)	9.8 (88%)		
Worton et al. (2007)	12.3 (74%)	12.1 (68%)	11.9 (75%)	11.8 (86%)	11.6 (104%)		
EDGAR 32/FT2000	11.8 (71%)	11.7 (66%)	11.0 (69%)	10.0 (74%)	11.3 (102%)		
EDGAR v4 (2009)	14.3 (86%)	13.7 (77%)	14.1 (89%)	13.3 (98%)	11.7 (105%)	10.4 (95%)	10.6 (101%)[a]
IAI Anode Surveys (only Al production)				9.8 (72%)	7.7 (69%)	5.6 (51%)	4.0 (38%)
UNFCCC Annex I countries[b]				8.3 (61%)	7.7 (70%)	5.5 (50%)	

[a] EDGAR v4 (2009) emission estimate for 2005 used for 2005–2008.

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

Table 7. Time averaged global C_2F_6 emission estimates.

	Time averaged C_2F_6 emissions (Gg/yr) and percentages of AGAGE emissions						
	1975–1979	1980–1984	1985–1989	1990–1994	1995–1999	2000–2004	2005–2008
This work	1.7±0.1	2.0±0.1	2.1±0.1	2.2±0.2	2.7±0.2	2.9±0.2	2.3±0.1
Harnisch et al. (1995)	2.0 (96%) (1978–1995)						
Harnisch et al. (1996b)	1.9 (88%) (1982–1996)						
Khalil et al. (2003)	1.6 (97%)	1.9 (96%)	2.0 (93%)	1.7 (75%)	2.0 (75%)		
Worton et al. (2007)	0.9 (55%)	0.9 (47%)	1.1 (50%)	1.6 (74%)	2.2 (82%)		
EDGAR 32/FT2000	1.2 (70%)	1.2 (61%)	1.2 (56%)	1.3 (58%)	2.2 (83%)		
EDGAR v4 (2009)	1.7 (102%)	1.9 (98%)	2.1 (100%)	2.0 (90%)	2.2 (82%)	2.3 (80%)	1.8 (76%)[a]
IAI Anode Surveys (10.2% of CF_4) (only Al production)				1.0 (46%)	0.8 (29%)	0.6 (20%)	0.4 (18%)
UNFCCC Annex I countries[b]				1.3 (59%)	1.3 (49%)	1.0 (33%)	

[a] EDGAR v4 (2009) emission estimates have been extrapolated beyond 2005 based on the 2005–2004 difference.

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

Table 8. Time averaged global C_3F_8 emission estimates.

	Time averaged C_3F_8 emissions (Gg/yr) and percentages of AGAGE emissions						
Global top-down estimates	1975–1979	1980–1984	1985–1989	1990–1994	1995–1999	2000–2004	2005–2008
This work	0.12±0.01	0.20±0.02	0.26±0.03	0.28±0.05	0.65±0.06	1.01±0.09	0.76±0.05
Khalil et al. (2003)	0.1 (52%)	(1978–1986)		0.3 (59%)	(1994–1997)		
Culbertson et al. (2004)	0.04 (26%) (1977–1982)	0.21 (90%) (1983–1987)	0.11 (40%) (1987–1992)		0.48 (104%) (1992–1997)		
EDGAR 32/FT2000	<0.01 (0.5%)	<0.01 (0.5%)	<0.01 (0.6%)	0.01 (4%)	0.12 (18%)		
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%)	

[a] EDGAR v4 (2009) emission estimates have been extrapolated beyond 2005 keeping 2005 refrigeration/air conditioning emissions (similar to 2000–2005) and extrapolating semiconductor/electronics and other F-gas use emissions beyond 2005 based on the 2005–2004 difference.

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

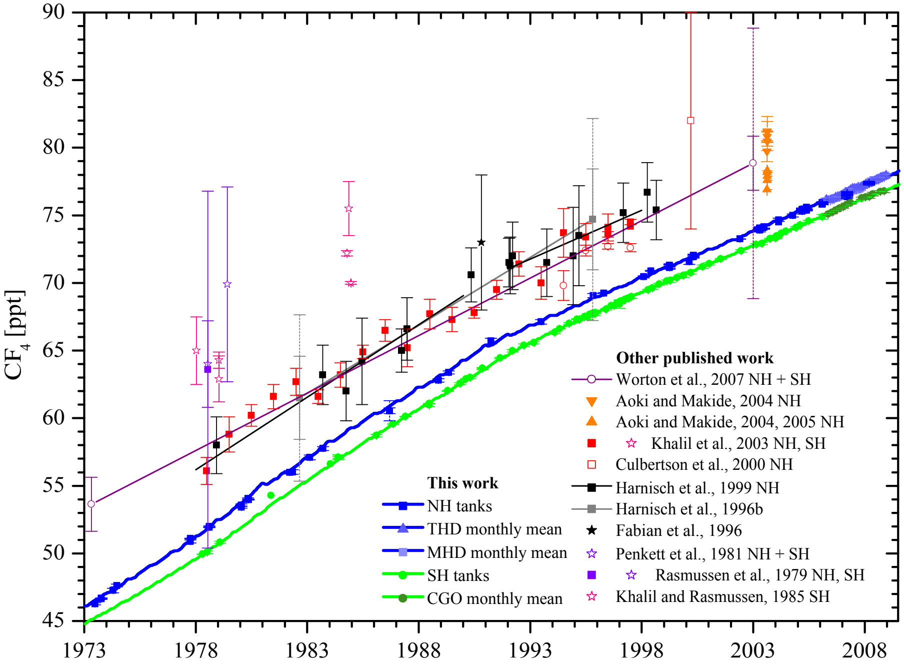

Fig. 1. AGAGE CF$_4$ abundances from archived Northern Hemisphere (NH) and Southern Hemisphere (SH) air samples and in situ measurements at Mace Head, Ireland (NH), Trinidad Head, California (NH), and Cape Grim, Tasmania (SH) and modeled 30–90° N and 30–90° S abundances all shown on the SIO-2005 calibration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

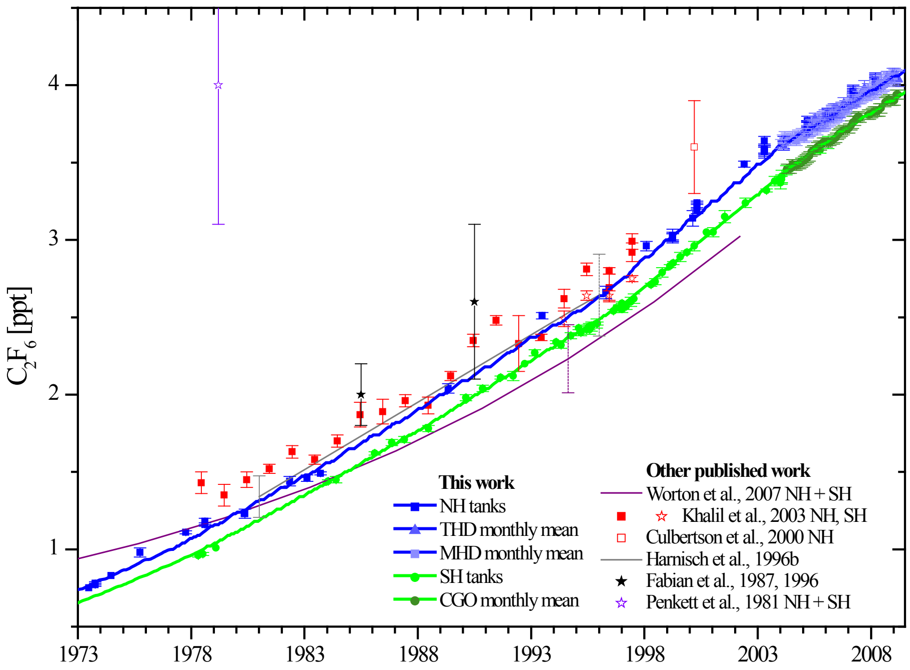

Fig. 2. AGAGE C_2F_6 abundances from archived Northern Hemisphere (NH) and Southern Hemisphere (SH) air samples and in situ measurements at Mace Head, Ireland (NH), Trinidad Head, California (NH) and Cape Grim, Tasmania (SH) and modeled 30–90° N and 30–90° S abundances all shown on the SIO-2007 calibration scale compared to previous observations. Uncertainty estimates for the MPAE 86 and UEA scales are indicated as additional dashed error bars. For the SIO-2007 scale they are is similar to the shown measurement precisions (~1–2%).

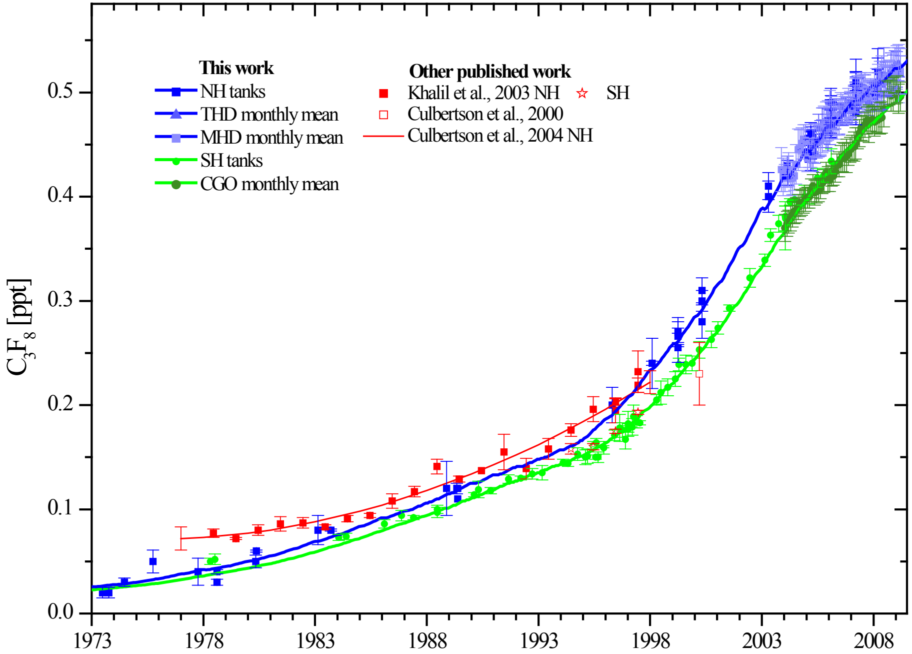

Fig. 3. AGAGE C_3F_8 abundances from archived Northern Hemisphere (NH) and Southern Hemisphere (SH) air samples and in situ measurements at Mace Head, Ireland (NH), Trinidad Head, California (NH), and Cape Grim, Tasmania (SH) and modeled 30–90° N and 30–90° S abundances all shown on the SIO-2007 scale compared to previous observations. The SIO-2007 calibration scale uncertainty estimate (~1–2%) is similar to the shown precisions.

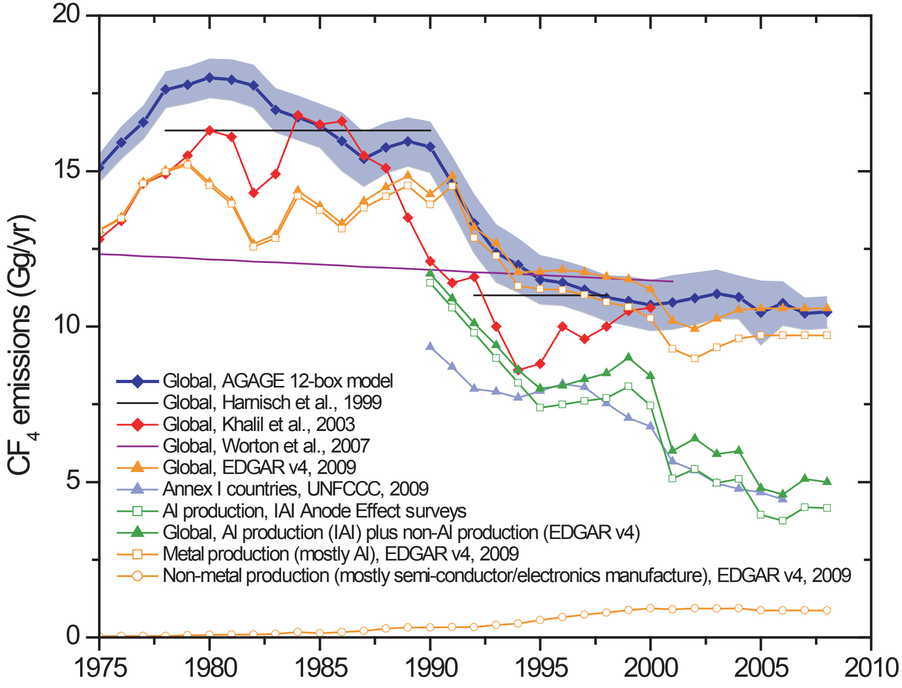

Fig. 4. Global CF_4 emissions from the inversion of AGAGE atmospheric data with the AGAGE 2-D 12-box model compared to the emissions reported by Harnisch et al. (1999), Khalil et al. (2003), Worton et al. (2007), the EDGAR v4 (2009) emission database, and Annex I countries (UNFCCC, 2009, Table S1, see http://www.atmos-chem-phys-discuss.net/10/6485/2010/acpd-10-6485-2010-supplement.pdf). Also shown are estimates of CF_4 emissions from Al production (IAI Anode Effect surveys), a global CF_4 emission estimate as the sum of these Al production CF_4 emissions and non-metal production related CF_4 emissions (EDGAR v4, mostly semiconductor/electronics manufacture), and the EDGAR v4 estimates for CF_4 emissions from metal production (mostly Al) and non-metal production. 2005 EDGAR v4 estimates have been used for 2005–2008.

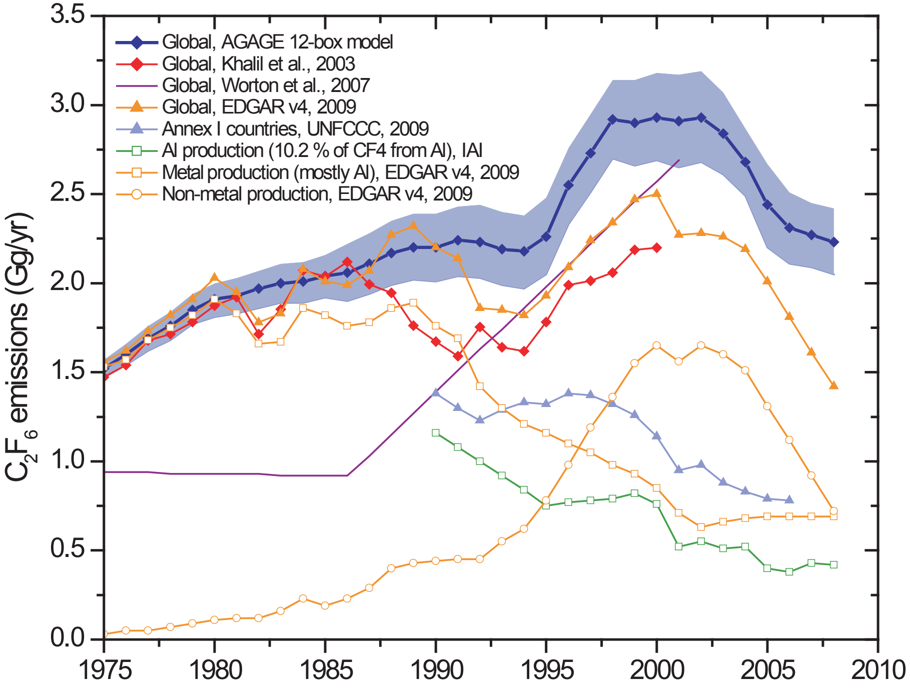

Fig. 5. Global C_2F_6 emissions from the inversion of AGAGE atmospheric data with the AGAGE 2-D 12-box model compared to the emissions reported by Khalil et al. (2003), Worton et al. (2007), the EDGAR v4 (2009) emission database, and Annex I countries (UNFCCC, 2009, Table S1, see http://www.atmos-chem-phys-discuss.net/10/6485/2010/acpd-10-6485-2010-supplement.pdf). Also shown are estimates of C_2F_6 emissions from Al production (10.2% of Al-production CF_4 emissions, IAI Anode Effect surveys), metal production (mostly Al, EDGAR v4, 2009), and non-metal production (EDGAR v4, 2009, >97% semiconductor/electronics manufacture). The EDGAR v4 estimates have been extrapolated beyond 2005 based on the 2005–2004 difference.

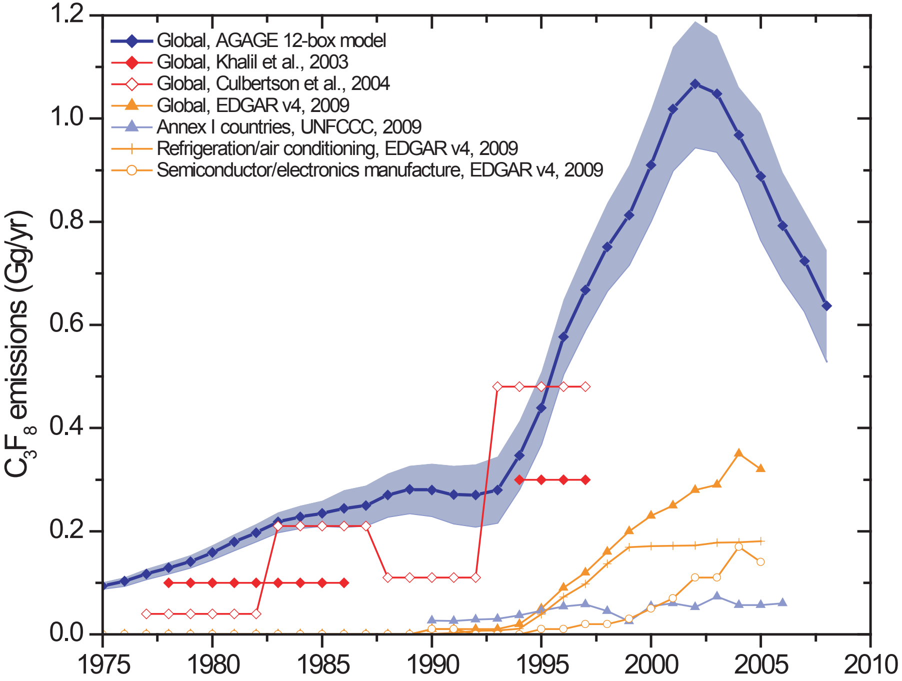

Fig. 6. Global C_3F_8 emissions from the inversion of AGAGE atmospheric data with the AGAGE 2-D 12-box model compared to emissions reported by Khalil et al. (2003), Culbertson et al., 2004), the EDGAR v4 (2009) emission database, and Annex I countries (UNFCCC, 2009, Table S1, see http://www.atmos-chem-phys-discuss.net/10/6485/2010/acpd-10-6485-2010-supplement.pdf). Also shown are EDGAR v4 emission estimates for refrigeration/air conditioning and semiconductor/electronics manufacture.