Global emission estimates and radiative impact of $\text{C}_4\text{F}_{10}$, $\text{C}_5\text{F}_{12}$, $\text{C}_6\text{F}_{14}$, $\text{C}_7\text{F}_{16}$ and $\text{C}_8\text{F}_{18}$

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Abstract

Global emission estimates based on new atmospheric observations are presented for the acyclic high molecular weight perfluorocarbons (PFCs): decafluorobutane (C$_{4}$F$_{10}$), dodecafluoropentane (C$_{5}$F$_{12}$), tetradecafluoroxythane (C$_{6}$F$_{14}$), hexadecafluorooctane (C$_{7}$F$_{16}$) and octadecafluorooctane (C$_{8}$F$_{18}$). Emissions are estimated using a 3-dimensional chemical transport model and an inverse method that includes a growth constraint on emissions. The observations used in the inversion are based on newly measured archived air samples that cover a 39-yr period, from 1973 to 2011, and include 36 Northern Hemispheric and 46 Southern Hemispheric samples (Ivy et al., 2012). The derived emission estimates show that global emission rates were largest in the 1980s and 1990s for C$_{4}$F$_{10}$ and C$_{5}$F$_{12}$, and in the 1990s for C$_{6}$F$_{14}$, C$_{7}$F$_{16}$ and C$_{8}$F$_{18}$. After a subsequent decline, emissions have remained relatively stable, within 20%, for the last 5 yr. Bottom-up emission estimates are available from the Emission Database for Global Atmospheric Research version 4.2 (EDGARv4.2) for C$_{4}$F$_{10}$, C$_{5}$F$_{12}$, C$_{6}$F$_{14}$ and C$_{7}$F$_{16}$, and inventories of C$_{4}$F$_{10}$, C$_{5}$F$_{12}$ and C$_{6}$F$_{14}$ are reported to the United Nations’ Framework Convention on Climate Change (UNFCCC) by Annex 1 countries that have ratified the Kyoto Protocol. The atmospheric measurement based emission estimates are 20 times larger than EDGARv4.2 for C$_{4}$F$_{10}$ and over three orders of magnitude for C$_{5}$F$_{12}$. The derived emission estimates for C$_{6}$F$_{14}$ largely agree with the bottom-up estimates from EDGARv4.2. Moreover, the C$_{7}$F$_{16}$ emission estimates are comparable to those of EDGARv4.2 at their peak in the 1990s, albeit significant underestimation for the other time periods. There are no bottom-up emission estimates for C$_{8}$F$_{18}$, thus the emission rates reported here are the first for C$_{8}$F$_{18}$. The reported inventories for C$_{4}$F$_{10}$, C$_{5}$F$_{12}$ and C$_{6}$F$_{14}$ to UNFCCC are five to ten times lower than those estimated in this study. In addition, we present measured infrared absorption spectra for C$_{7}$F$_{16}$ and C$_{8}$F$_{18}$, and estimate their radiative efficiencies and global warming potentials (GWPs). We find that C$_{8}$F$_{18}$’s radiative efficiency is similar to trifluoromethyl sulfur pentafluoride’s (SF$_{5}$CF$_{3}$) at 0.57 W m$^{-2}$ ppb$^{-1}$, which is the highest
Radiative efficiency of any measured atmospheric species. Using the 100-yr time horizon GWPs, the high molecular weight perfluorocarbons studied here contributed up to 15.4% of the total PFC emissions in CO₂ equivalents in 1997 and 6% of the total PFC emissions in 2009.

1 Introduction

Perfluorocarbons (PFCs) are potent greenhouse gases due to their long lifetimes and strong absorption in the infrared atmospheric window region, resulting in global warming potentials (GWPs) on a 100-yr time horizon of three to four orders of magnitude higher than that of carbon dioxide (CO₂) (see Table 1) (Forster et al., 2007). Subsequently, PFCs are considered to have a nearly permanent effect on the Earth’s radiative budget, when human time scales are considered. PFCs are included as one of the six classes of greenhouse gases under the Kyoto Protocol to the United Nations’ Framework Convention on Climate Change (UNFCCC).

Atmospheric observations and global emission estimates based on atmospheric measurements are available for the lower molecular weight PFCs: tetrafluoromethane (CF₄), hexafluoroethane (C₂F₆), octafluoropropane (C₃F₈) and octafluorocyclobutane (c–C₄F₈) (Mühle et al., 2010; Oram et al., 2012). The lower molecular weight PFCs are primarily emitted from the production of aluminum and usage in the semiconductor industry. Efforts are being made by both industries to reduce these emissions (International Aluminium Institute, 2011; Semiconductor Industry Association, 2001; World Semiconductor Council, 2005). Furthermore, CF₄ and C₂F₆ have a natural abundance due to a lithospheric source (Deeds et al., 2008; Harnisch et al., 1996a,b; Mühle et al., 2010). The global emission estimates by Mühle et al. (2010) and Oram et al. (2012) for the lower molecular weight PFCs concluded that bottom-up emission estimates, based on production information and end usage, were underestimated as compared to estimates constrained by atmospheric observations, particularly for C₃F₈ and c–C₄F₈.
These studies illustrate the valuable constraint atmospheric observations provide in independently estimating emissions for the verification of bottom-up emission estimates.

Bottom-up emission estimates are provided by the Emission Database for Global Atmospheric Research version 4.2 (EDGARv4.2) for the high molecular weight PFCs: decafluorobutane ($\text{C}_4\text{F}_{10}$), dodecafluoropentane ($\text{C}_5\text{F}_{12}$), tetradecafluorohexane ($\text{C}_6\text{F}_{14}$) and hexadecafluoroheptane ($\text{C}_7\text{F}_{16}$) from 1970 to 2008 (ER-JRC/PBL, 2009). Furthermore, $\text{C}_4\text{F}_{10}$, $\text{C}_5\text{F}_{12}$ and $\text{C}_6\text{F}_{14}$ emissions are reported from 1990 to 2009 to UNFCCC by Annex 1 countries that have ratified the Kyoto Protocol (UNFCCC, 2011). However, no emission data are available for octadecafluorooctane ($\text{C}_8\text{F}_{18}$).

Since the early 1990s, these higher molecular weight PFCs have had a relatively minor role as replacements for ozone depleting substances (ODS), which are regulated under the Montreal Protocol (Harvey, 2000). The most significant emission source of the high molecular weight PFCs are from their use as solvents in electronics and precision cleaning, which was approved under the Significant New Alternatives Policy (SNAP) program (Tsai, 2009; Air and Radiation Global Programs Division, 2006). There are also small niche markets for $\text{C}_4\text{F}_{10}$ and $\text{C}_6\text{F}_{14}$ as fire suppressants (Forte, Jr. et al., 2003; Kopylov, 2002; Tsai, 2009) and $\text{C}_4\text{F}_{10}$, $\text{C}_5\text{F}_{12}$ and $\text{C}_6\text{F}_{14}$ as refrigerants (ER-JRC/PBL, 2009; Schwaab et al., 2005; Tsai, 2009). Because of the PFCs’ large GWPs, emissions of these high molecular weight PFCs as ODS replacements are expected to be decreasing as they are being replaced with lower GWP alternatives (Harvey, 2000; United Nations Environment Programme, 1999).

The PFCs, which are liquid at room temperature, $\text{C}_5\text{F}_{12}$-$\text{C}_8\text{F}_{18}$ are additionally being used in the semiconductor manufacturing industry as heat transfer fluids and in vapor phase reflow soldering (3M Electronics Markets Materials Division, 2003; Tsai, 2009; Tuma and Tousignant, 2001). This emission source is a first-of-a-kind for fluorinated compounds (Tuma and Tousignant, 2001). While the semiconductor industry is making efforts to reduce PFC emissions, their efforts are focused on reducing emissions of the lower molecular weight PFCs. Therefore emission estimates based on atmospheric
observations of the high molecular weight PFCs are valuable for determining if these industries are indeed reducing all PFC emissions.

Laube et al. (2012) provided global emission estimates using a 2-dimensional model and atmospheric observations for C₄F₁₀, C₅F₁₂, C₆F₁₄ and C₇F₁₆. However, the emission estimates by Laube et al. (2012) were determined qualitatively and not constrained by an inverse method, and therefore their emissions were not optimally determined. In this study, we present global annual emission estimates for the high molecular weight PFCs, C₄F₁₀, C₅F₁₂, C₆F₁₄, C₇F₁₆ and C₈F₁₈, based on new atmospheric measurements presented in Ivy et al. (2012). Emissions are estimated using a 3-dimensional chemical transport model (CTM), the Model of Ozone and Related Tracers (MOZARTv4.5) and an inverse method, in which the atmospheric observations and an independent estimate of the emission growth rates are used as constraints (Rigby et al., 2011). The derived emissions based on atmospheric measurements are compared to the available bottom-up emission data from EDGARv4.2 and the inventories reported to UNFCCC. Furthermore, we present measured infrared (IR) absorption spectra for C₇F₁₆ and C₈F₁₈ in order to provide estimates of their GWPs. Thus, we provide an updated total of the radiative impact of global PFC emissions in CO₂ equivalents from 1978 to 2009, now including the high molecular weight PFCs.

2 Inverse modeling

2.1 Observations

The atmospheric observations of the high molecular weight PFCs used to constrain the derived emission estimates are based on archived air samples that were measured using the Advanced Global Atmospheric Gases Experiment (AGAGE) “Medusa” systems and cover a time period from 1973 to 2011, see Ivy et al. (2012) for details. The atmospheric histories of the high molecular weight PFCs, shown in Fig. 1, are based on measurements of 36 Northern Hemisphere (NH) archived air samples, filled primarily
at Trinidad Head, California (41.05° N, 124.05° W), and 46 Southern Hemisphere (SH) archived air samples, filled at Cape Grim, Tasmania, Australia (40.68° S, 144.69° E). For this modeling study, the observations were assumed to be representative of the monthly mean hemispheric background tropospheric air. This is a valid assumption given that the archived air samples were filled under baseline conditions.

Associated with each observation is an estimate of its uncertainty, which includes the estimated uncertainties associated with the measurements, the sampling frequency, grid cell model-mismatch and use of repeated dynamics when applicable, see Eq. (1) (Rigby et al., 2010). The measurement uncertainty, \( \sigma_{\text{measurement}} \), is the repeatability of each archived air sample measurement and is taken as the 1-\( \sigma \) standard deviation of the repeat sample measurements. The sampling frequency uncertainty, \( \sigma_{\text{sampling frequency}} \), provides a measure of the uncertainty in our assumption that a single flask is representative of the monthly mean baseline variability. Since high frequency data are not available, the sampling frequency uncertainty was estimated as the standard deviation of daily modeled output from the CTM over one month at the observation grid cell. The model-mismatch error, \( \sigma_{\text{mismatch}} \), is an estimate of the uncertainty in the assumption that the model grid cell is representative of a single point measurement. We estimated the model-mismatch error using the CTM as the 1-\( \sigma \) standard deviation of the surrounding eight grid cells and the grid cell that contains the observation location from the mean of all nine cells (Chen and Prinn, 2006). Reanalysis meteorological data are not available for years prior to 1990 for use in the CTM; therefore, we used repeated meteorological data from 1990 for the years from 1971 to 1989 in the CTM and 2008 for the years from 2009 to 2011. In order to characterize the uncertainty in this use of repeated dynamics, \( \sigma_{\text{dynamics}} \), a one year simulation was run multiple times with different meteorological data from other years, while the emissions and initial conditions were held constant (Rigby et al., 2010). This introduced a mean uncertainty of 5% at the observation grid cells and was included in the observational uncertainty. Lastly, observations that were below the detection limit of the instruments
were assigned a minimum uncertainty equal to that of the detection limit.

\[
\sigma^2_{\text{observational}} = \sigma^2_{\text{measurement}} + \sigma^2_{\text{sampling frequency}} + \sigma^2_{\text{mismatch}} + \sigma^2_{\text{dynamics}} \tag{1}
\]

2.2 Bottom-up emission estimates

Bottom-up emission estimates are available from EDGARv4.2 (ER-JRC/PBL, 2009). EDGARv4.2 has global annual emission estimates by source for \(C_4F_{10}, C_5F_{12}, C_6F_{14}\) and \(C_7F_{16}\) from 1970 to 2008, see Fig. 2, and on a 0.1° longitude by 0.1° latitude grid-ded data, with non-zero emissions starting in 1971 for \(C_4F_{10}\), 1986 for \(C_5F_{12}\), 1980 for \(C_6F_{14}\) and 1986 for \(C_7F_{16}\). There are no EDGARv4.2 estimates available for \(C_8F_{18}\), therefore \(C_7F_{16}\) estimates were used as a proxy. This is under the assumption that as \(C_7F_{16}\) and \(C_8F_{18}\) have similar properties, they will most likely have similar emission sources. Furthermore, as the archived samples are assumed to be representative of well-mixed background air, the emission estimates will not be sensitive to hemispheric relative spatial distributions. For 2009 to 2011, the emissions were linearly interpolated from the 2007 to 2008 data. The annual 0.1° longitude by 0.1° latitude emissions were regridded to a horizontal resolution of 2.8° longitude by 2.8° latitude for use in the CTM. Inventories for \(C_4F_{10}, C_5F_{12}\) and \(C_6F_{14}\) are also reported to UNFCCC by Annex 1 countries that have ratified the Kyoto Protocol. However as the reported inventories to UNFCCC are not global, we used the EDGARv4.2 data in the CTM to produce the reference runs and to estimate the sensitivity of the modeled mole fractions to changes in emissions.

2.3 Chemical transport model

The Model of Ozone and Related Tracers (MOZARTv4.5) is a 3-dimensional chemical transport model (Emmons et al., 2010). MOZARTv4.5 was run offline to produce the reference run of modeled atmospheric mole fractions, using the emissions described in Sect. 2.2, and to estimate the sensitivities of the atmospheric mole fractions to emission perturbations. Meteorological data were provided from the National Centers for...
Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) reanalysis (Kalnay et al., 1996). The NCEP/NCAR reanalysis for use in MOZARTv4.5 are available from 1990 to 2008 every 6 h at a horizontal resolution of 1.8° longitude by 1.8° latitude and with 28 vertical levels in sigma coordinates, from the surface to 3 hPa. MOZARTv4.5 interpolated the meteorological data to a resolution of 2.8° longitude by 2.8° latitude, which was the chosen horizontal resolution of the model runs. For years prior to 1990, NCEP/NCAR reanalysis data from 1990 were used repeatedly; and for years after 2008, the 2008 meteorological data were repeated. The PFCs were treated as tracers and no chemistry was input into MOZART; this is a reasonable assumption given their lifetimes are on the order of thousands of years (Ravishankara et al., 1993).

A zero initial condition field was assumed for all of the high molecular weight PFCs, with an initial year based on EDGARv4.2’s first non-zero emissions of 1971 for C₄F₁₀, 1986 for C₅F₁₂, C₇F₁₆ and C₈F₁₈, and 1980 for C₆F₁₄. The upwind cells of the observation stations were chosen in MOZARTv4.5, as the observations are assumed to be representative of background air (Rigby et al., 2010).

In order to estimate the sensitivities of the atmospheric mole fractions to changes in emission rates, MOZARTv4.5 was run with annual emissions increased by 10% from the reference run for one year. In the subsequent year, the emissions were returned to those of the reference run. This provided an estimate of the sensitivities of mole fractions at the observation grid cells to annual emission changes. Due to the computational expense of running MOZARTv4.5, these sensitivities were only tracked in the model for two years, and then the values were estimated to decay exponentially, with a one year decay time, to a globally mixed background value.

### 2.4 Inverse method

To derive global emissions, we used an inverse method that included constraints by the atmospheric observations and an independent estimate of the annual growth in emissions (Rigby et al., 2011). Often a minimum variance Bayesian approach is taken for atmospheric measurement based emission estimates while using an independent
estimate of absolute emissions, also known as prior, as a constraint. However, if the prior emission information is largely biased, as is the case for $C_4F_{10}$ and $C_5F_{12}$, a large uncertainty is often assumed on the prior. This results in the prior providing little information on the derived emissions if observations are available. Alternatively, if observations are not available for a certain year, then the derived emissions can exhibit unphysical fluctuations due to the biased prior constraining the emissions. The growth-based Bayesian inverse approach, which incorporates the growth rate of emissions as prior information instead of absolute emission rates, overcomes some of these potential biases (Rigby et al., 2011). This inverse method acts to minimize the residuals of the atmospheric observations from the modeled mole fractions and the growth rate in the derived emissions from an independent estimate of the emission growth rate. These two constraints are weighted by their relative uncertainties in determining the optimal solution. Here, the observations were weighted by their observational error, described in Sect. 2.1. The assumed independent growth rate was the annual average growth rate in emissions for each species from EDGARv4.2. EDGARv4.2 does not provide an uncertainty estimate and because of the underestimation in $C_4F_{10}$ and $C_5F_{12}$ in the EDGARv4.2 estimates, the error assumed on the growth rate for $C_4F_{10}$ and $C_5F_{12}$ was the mean growth rate in emissions for $C_4F_{10}$, $C_5F_{12}$, $C_6F_{14}$ and $C_7F_{16}$ from EDGARv4.2. For $C_6F_{14}$, the assumed error was the mean growth rate in emissions from 1980 to 2008 from EDGARv4.2 for $C_6F_{14}$, and likewise for $C_7F_{16}$ and $C_8F_{18}$. Due to the low temporal frequency of the observations, only globally averaged emissions were resolved.

The year of emission onset in EDGARv4.2 appears to be later than the observations suggest – as observations are non-zero in earlier years. Therefore, an initial condition was also solved for in the inversion. The initial condition was applied globally; as the first SH observation is 5 yr after the first NH observation, this should not have a large influence on the derived emissions. In addition, we included an estimate of the uncertainty in the use of repeated dynamics in the derived emission estimates using a Monte Carlo approach, where the inversion was repeated 1000 times with randomly
varied sensitivities of the modeled mole fractions to perturbations in emissions. The distribution of varied sensitivities was estimated by running the model multiple times with meteorological data from different years and calculating the mole fraction sensitivities, while the emissions and initial conditions were held constant (Rigby et al., 2010). This error was found to be relatively small compared to the error propagated through the inversion, and was added in quadrature to give the final estimate of emission uncertainty. The uncertainty on emissions was estimated from the diagonal elements of the error covariance matrix and is based on the relative weighting of the uncertainty associated with the observations as compared to the uncertainty associated with the assumed growth rate constraint on emissions (Rigby et al., 2011).

3 Radiative efficiencies of C$_7$F$_{16}$ and C$_8$F$_{18}$

3.1 Infrared absorption cross-sections

Roehl et al. (1995) reported infrared absorption cross-sections and GWPs for CF$_4$, C$_2$F$_6$, C$_3$F$_8$, C$_4$F$_{10}$, C$_5$F$_{12}$ and C$_6$F$_{14}$ while Bravo et al. (2010), more recently, similarly for C$_8$F$_{18}$. In the present work, we measured infrared absorption spectra of C$_7$F$_{16}$ and C$_8$F$_{18}$ using Fourier Transform Infrared (FTIR) spectroscopy. To the best of our knowledge there are no previously published infrared absorption spectrum measurements for C$_7$F$_{16}$ available.

The C$_7$F$_{16}$ ($\geq 98\%$) and C$_8$F$_{18}$ ($\geq 99\%$) samples were purchased from Synquest Laboratories. These samples were vacuum distilled to remove non-condensables prior to use. Various dilute gas mixtures of the samples in a Helium (He) bath gas were prepared manometrically in 12-l Pyrex bulbs for use in the infrared spectrum measurements. Absorption spectra were measured between 500 and 4000 cm$^{-1}$ at a spectral resolution of 1 cm$^{-1}$. Spectra were obtained using two different pathlength absorption cells: a single-pass 16 cm long cell and a low-volume multi-pass cell (750 cm$^3$, 485 cm optical pathlength). Infrared absorption band strengths (absorption cross-sections)
were obtained using Beer’s law with spectra recorded over a range of sample concentrations at various bath gas pressures. The infrared spectra of C\textsubscript{7}F\textsubscript{16} and C\textsubscript{8}F\textsubscript{18} were independent of bath gas pressure for pressures between 20 and 600 Torr (He bath gas). The sample concentrations in the infrared absorption cell were varied over the range (0.10–8.28) \times 10^{15} \text{ mol cm}^{-3} for C\textsubscript{7}F\textsubscript{16} and (0.05–7.08) \times 10^{15} \text{ mol cm}^{-3} for C\textsubscript{8}F\textsubscript{18}, where the sample concentrations were determined using absolute pressure measurements and the known mixing ratio.

Figure 3 shows the infrared absorption spectra of C\textsubscript{7}F\textsubscript{16} and C\textsubscript{8}F\textsubscript{18}. The C\textsubscript{7}F\textsubscript{16} and C\textsubscript{8}F\textsubscript{18} spectra show weak absorption between 500 and 1000 cm\textsuperscript{-1}, but strong absorption bands between 1000 and 1400 cm\textsuperscript{-1}, where the integrated absorption band strengths were determined to be (3.61 \pm 0.21) \times 10^{-16} \text{ cm}^{2} \text{ mol}^{-1} \text{ cm}^{-1} for C\textsubscript{7}F\textsubscript{16} (1075–1375 cm\textsuperscript{-1}) and (4.02 \pm 0.24) \times 10^{-16} \text{ cm}^{2} \text{ mol}^{-1} \text{ cm}^{-1} for C\textsubscript{8}F\textsubscript{18} (1100–1400 cm\textsuperscript{-1}). The quoted uncertainties are at the 2-σ (95 % confidence) level and include estimated systematic uncertainties. The infrared absorption spectra data of C\textsubscript{7}F\textsubscript{16} and C\textsubscript{8}F\textsubscript{18} are provided in the Supplement.

3.2 Radiative efficiencies

In order to estimate the relative change in radiative forcing per change in atmospheric concentrations, the radiative efficiencies were estimated for C\textsubscript{7}F\textsubscript{16} and C\textsubscript{8}F\textsubscript{18} using the spectra measured here and the method given by Pinnock et al. (1995). The radiative efficiency for C\textsubscript{7}F\textsubscript{16} and C\textsubscript{8}F\textsubscript{18} are 0.48 and 0.57 W m\textsuperscript{-2} ppb\textsuperscript{-1}, respectively, see Table 1. The radiative efficiency for C\textsubscript{8}F\textsubscript{18} is approximately equal to that of trifluoromethyl sulfur pentafluoride (SF\textsubscript{5}CF\textsubscript{3}), which is the highest of any measured atmospheric species (Forster et al., 2007).

The radiative efficiencies reported here are in reasonably good agreement, within 7 %, with those estimated by Bravo et al. (2010). The infrared measurements by Bravo et al. (2010) for C\textsubscript{8}F\textsubscript{18} were limited to the spectral range 700–1400 cm\textsuperscript{-1}. A radiative efficiency value, based on our measurements, of 0.53 W m\textsuperscript{-2} ppb\textsuperscript{-1} for C\textsubscript{8}F\textsubscript{18} can be
obtained if a spectral range of 700–1400 cm\(^{-1}\) is used. Therefore we attribute the difference between the reported and measured value for C\(_8\)F\(_{18}\) to the different spectral ranges of the measurements. The radiative efficiencies by Bravo et al. (2010), based on theoretical calculations and that include a larger spectral range 0–2500 cm\(^{-1}\), are closer to our results for C\(_8\)F\(_{18}\), with a difference of 3.6%. Bravo et al. (2010) did not measure the infrared spectra of C\(_7\)F\(_{16}\) and provide a theoretical calculation of C\(_7\)F\(_{16}\)’s radiative efficiency as 0.45 W m\(^{-2}\) ppb\(^{-1}\), which is in good agreement with the results from the present work.

### 3.3 Global warming potential

Global warming potentials (GWPs) provide a measure of the climate impact of emissions of a trace gas relative to a reference gas, usually chosen as carbon dioxide (CO\(_2\)) (Forster et al., 2007; United Nations Environment Programme, 1999). The radiative efficiencies, along with an estimate of the species’ atmospheric lifetimes, allow for GWPs to be estimated. Following the standard method outlined by Forster et al. (2007), the GWPs were calculated for C\(_7\)F\(_{16}\) and C\(_8\)F\(_{18}\). No lifetimes have been estimated for C\(_7\)F\(_{16}\) and C\(_8\)F\(_{18}\). Ravishankara et al. (1993) determined that the major atmospheric removal pathway for the perfluoroalkanes, CF\(_4\)-C\(_6\)F\(_{14}\), was via photolysis by hydrogen Lyman-\(\alpha\) radiation (121.6 nm) with a possible minor pathway due to reaction with O(\(^1\)D). Based on the work by Ravishankara et al. (1993), we assume that C\(_7\)F\(_{16}\) and C\(_8\)F\(_{18}\) will have similar lifetimes, on the order of thousands of years, and have chosen a lifetime of 3000 yr for the GWP calculations, which is close to the lifetime of C\(_6\)F\(_{14}\). The GWPs for C\(_7\)F\(_{16}\) and C\(_8\)F\(_{18}\) are estimated to be 7900 and 8350 for a 100-yr time horizon with CO\(_2\) as the reference gas, see Table 1. As the expected lifetimes of C\(_7\)F\(_{16}\) and C\(_8\)F\(_{18}\) are much longer than the chosen time horizons, these GWP calculations are relatively insensitive to the assumed lifetime. To confirm this, a sensitivity analysis to the assumed lifetime in the GWP estimate was done following Shine et al. (2005).
Less than a 5% difference was found in the calculated 100-yr time horizon GWPs when using assumed lifetimes of 500 vs. 3000 or 3000 vs. 10,000 yr.

4 Results and discussion

The reference run of modeled mole fractions using the bottom-up estimates from EDGARv4.2 are lower than the atmospheric observations for the high molecular weight PFCs, see Fig. 1. In particular, the reference run produces modeled mole fractions that are 20 times and over a 1000 times too low for C₄F₁₀ and C₅F₁₂, respectively. For C₅F₁₂ this is due to the global annual emissions from EDGARv4.2 peaking at less than 0.1 t yr⁻¹, with the only emission source being use as refrigerants in the Ukraine. In contrast, the reference modeled mole fractions for C₆F₁₄ are similar to the observations, although the reference run is somewhat lower in the mid-1990s, suggesting an underestimation of emissions during this period. For C₇F₁₆ and C₈F₁₈, the reference is about 50% lower than atmospheric observations.

Using our inverse method, we provide new global emission estimates based on atmospheric observations. The derived emissions and their associated uncertainties are presented in Fig. 4 and Table 2. The derived emissions for C₄F₁₀ and C₅F₁₂ are relatively constant over the time period with an average emission rate and uncertainty of 196 ± 33 t yr⁻¹ and 171 ± 42 t yr⁻¹, respectively. The C₄F₁₀ and C₅F₁₂ emissions have the largest decline from 1999 to 2005. The EDGARv4.2 emissions are 20 and 1000 times lower than the derived emissions for C₄F₁₀ and C₅F₁₂, respectively. Furthermore, the EDGARv4.2 emission temporal profile is drastically different than those derived from the observations, with emissions in EDGARv4.2 being relatively lower in the 1980s and then increasing with time.

In contrast, the derived emissions for C₆F₁₄ agree fairly well with EDGARv4.2. The C₆F₁₄ increase in emissions has a later onset, starting in the 1990s, than that of C₄F₁₀ and C₅F₁₂, and has a similar emission profile as that of C₃F₈, shown in Mühle et al.
Of the PFCs studied here, C$_6$F$_{14}$ has the largest emissions with a 1980 to 2010 average emission rate of $510 \pm 62$ t yr$^{-1}$.

The derived emissions for C$_7$F$_{16}$ and C$_8$F$_{18}$ are both higher than those of C$_7$F$_{16}$ in EDGARv4.2. Interestingly while the other high molecular weight PFC emissions have decreased in the past 10 to 20 yr, the derived emissions for C$_7$F$_{16}$ are relatively constant for the last ten years, with an average emission rate over the entire study period of $251 \pm 37$ t yr$^{-1}$. The average emission rate for C$_8$F$_{18}$ is $195 \pm 34$ t yr$^{-1}$.

Our derived emissions for C$_4$F$_{10}$ and C$_5$F$_{12}$ agree fairly well with those presented by Laube et al. (2012). However, we see discrepancies for C$_6$F$_{14}$ and C$_7$F$_{16}$. In particular, Laube et al. (2012) estimates lower emission rates from 1994 to 2001 than ours for C$_6$F$_{14}$. The C$_6$F$_{14}$ observations from Laube et al. (2012) agree well with those presented in Ivy et al. (2012) in the early 1980s and 1990s; however after this time period the observations by Laube et al. (2012) are lower than those in Ivy et al. (2012). This is most likely due to a calibration scale difference, with that of Laube et al. (2012) estimating lower mole fractions than Ivy et al. (2012), and possible nonlinearities in the early archive measurements. We see a general underestimation of C$_7$F$_{16}$ emissions by Laube et al. (2012) compared with those estimated in this study. This is most likely due to the lower calibration scale by Laube et al. (2012) as compared with Ivy et al. (2012). Laube et al. (2012) used an 85% $n$-isomer of C$_7$F$_{16}$ for their calibration scale and subsequently estimate an atmospheric mole fraction in 2010 that is 13% lower. Laube et al. (2012) did not present atmospheric measurements or emission estimates for C$_8$F$_{18}$. Furthermore as no bottom-up estimates are available either, the C$_8$F$_{18}$ emissions derived in this study are the first published estimates.

Overall the UNFCCC reported inventories are five to ten times lower than the emissions derived based on the observations for C$_4$F$_{10}$, C$_5$F$_{12}$ and C$_6$F$_{14}$. In general, the UNFCCC emission inventories could be considered a lower bounds on global emissions as they do not include some major greenhouse gas emitters. Both C$_7$F$_{16}$ and C$_8$F$_{18}$ are not reported to UNFCCC; however based on our results, their emissions are larger than those of C$_4$F$_{10}$ and C$_5$F$_{12}$ and should be considered in future inventories.
MOZARTv4.5 was run using the derived emissions and produced modeled mole
fractions that were much closer to the observations (as required in the inversion), see
Fig. 1. Figure 5 shows the residuals of the final modeled mole fractions using the
derived emissions to the observations. Most of the residuals are within the estimated
observational error and no significant trends in the residuals are found, confirming that
the derived emissions represent an improved estimate.

Using the 100-yr time horizon GWPs, we provide an update to the total annual global
PFC emissions in CO₂ equivalents (Fig. 6). CF₄, C₂F₆ and c–C₄F₈ contribute the most
to the radiative forcing of the PFC emissions. However, we find that the high molecular
weight PFCs contribute significantly to the total PFC budget, with the C₆F₁₄ emissions
being comparable to those of C₃F₈. Previous estimates of the radiative forcing of PFC
emissions in 2009, which only included CF₄, C₂F₆, C₃F₈ and c–C₄F₈, are 111 600 Gg
CO₂ equivalents in 2009 (Mühle et al., 2010; Oram et al., 2012); inclusion of the high
molecular weight PFCs increases this number by 6 % to 118 700 Gg CO₂-eq.

The high molecular weight PFC emissions from 1973 to 2010 have contributed to
a total cumulative forcing of 400 000 Gg of CO₂ equivalents and their 2010 emission
rates are comparable to the release of 7300 Gg of CO₂. The largest contribution of the
high molecular weight PFCs to the global PFC emission budget was in 1997, when they
contributed 15.4 % of the total emissions in 1997. Since 1997, the relative contribution
to the global emissions of the high molecular weight PFCs has decreased, most likely
due to their replacement with low GWP alternatives (Office of Air and Radiation and
Office of Atmospheric Programs, 2006).

5 Conclusions

In this study, global emission estimates from 1973 to 2010 have been presented for
C₄F₁₀, C₅F₁₂, C₆F₁₄, C₇F₁₆ and C₈F₁₈ using new atmospheric observations and an
independent growth constraint on emissions. We find a significant underestimation
by EDGARv4.2 for C₄F₁₀ and C₅F₁₂, further illustrating the benefit of atmospheric
observations based emission estimates in verifying bottom-up emission estimates. Additionally, the reported inventories to UNFCCC by Annex 1 countries that have ratified the Kyoto Protocol are generally five to ten times lower than the derived emission rates for C$_4$F$_{10}$, C$_5$F$_{12}$ and C$_6$F$_{14}$. However the derived emissions are global, therefore this discrepancy cannot be attributed to individual countries. These large discrepancies between the derived and bottom-up estimates highlight the need for more transparent and accurate reporting of emissions. Interestingly, the UNFCCC reported inventories show similar temporal trends as the derived emissions, suggesting the UNFCCC methodology may be a good platform for emissions reporting.

Using the newly derived GWPs for C$_7$F$_{16}$ and C$_8$F$_{18}$, new estimates of the total radiative impact of all PFC emissions are an average 7% higher than previously reported for 1973 to 2009. The high molecular weight PFCs contributed most significantly to the global PFC emissions, up to 16% in the 1990s, suggesting a previous underestimation of the total radiative forcing from PFC emissions. While emissions have declined in the past 10 yr, because of their long lifetimes, PFCs are considered to have a nearly permanent effect on the Earth’s radiative budget on human timescales. Therefore, continued monitoring of atmospheric abundances is necessary to detect trends in emissions of these potent greenhouse gases.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/12987/2012/acpd-12-12987-2012-supplement.zip.

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Table 1. Lifetimes, radiative efficiencies and global warming potentials of C₄F₁₀, C₅F₁₂, C₆F₁₄, C₇F₁₆ and C₈F₁₈.

<table>
<thead>
<tr>
<th>Species</th>
<th>Lifetime [yr]</th>
<th>Radiative efficiencies [W m⁻² ppb⁻¹]</th>
<th>20-yr horizon</th>
<th>100-yr horizon</th>
<th>500-yr horizon</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>C₄F₁₀</td>
<td>2600</td>
<td>0.33</td>
<td>6330</td>
<td>8860</td>
<td>12 500</td>
<td>Forster et al. (2007)</td>
</tr>
<tr>
<td>C₅F₁₂</td>
<td>4100</td>
<td>0.41</td>
<td>6510</td>
<td>9160</td>
<td>13 300</td>
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</tr>
<tr>
<td>C₆F₁₄</td>
<td>3200</td>
<td>0.49</td>
<td>6600</td>
<td>9300</td>
<td>13 300</td>
<td>Forster et al. (2007)</td>
</tr>
<tr>
<td>C₇F₁₆</td>
<td>(3000)</td>
<td>0.48</td>
<td>5700</td>
<td>7900</td>
<td>11 300</td>
<td>This Study</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>0.45</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Bravo et al. (2010)</td>
</tr>
<tr>
<td>C₈F₁₈</td>
<td>(3000)</td>
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<td>6000</td>
<td>8350</td>
<td>11 900</td>
<td>This Study</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>0.50</td>
<td>5280</td>
<td>7390</td>
<td>10 500</td>
<td>Bravo et al. (2010)</td>
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Table 2. Annual mean global emission rates and uncertainties for $C_4F_{10}$, $C_5F_{12}$, $C_6F_{14}$, $C_7F_{16}$ and $C_8F_{18}$.

<table>
<thead>
<tr>
<th>Year</th>
<th>$C_4F_{10}$ [t yr$^{-1}$]</th>
<th>$C_5F_{12}$ [t yr$^{-1}$]</th>
<th>$C_6F_{14}$ [t yr$^{-1}$]</th>
<th>$C_7F_{16}$ [t yr$^{-1}$]</th>
<th>$C_8F_{18}$ [t yr$^{-1}$]</th>
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<tbody>
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<td>108 ± 16</td>
<td>147 ± 44</td>
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<td>129 ± 17</td>
<td>179 ± 43</td>
<td>183 ± 22</td>
<td>83 ± 30</td>
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<tr>
<td>1982</td>
<td>197 ± 23</td>
<td>152 ± 18</td>
<td>229 ± 43</td>
<td>188 ± 22</td>
<td>83 ± 29</td>
</tr>
<tr>
<td>1983</td>
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<td>174 ± 19</td>
<td>290 ± 43</td>
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</tr>
<tr>
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<td>211 ± 23</td>
<td>192 ± 20</td>
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</tr>
<tr>
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<td>162 ± 20</td>
<td>81 ± 26</td>
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<td>1986</td>
<td>213 ± 24</td>
<td>213 ± 21</td>
<td>289 ± 42</td>
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<td>561 ± 60</td>
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<td>102 ± 48</td>
<td>70 ± 52</td>
<td>345 ± 118</td>
<td>260 ± 56</td>
<td>60 ± 53</td>
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</table>
Fig. 1. MOZARTv4.5 model output at the observation grid cells (Northern Hemisphere – solid line and Southern Hemisphere – dashed line) for the reference run using emissions based on EDGARv4.2 (yellow lines) and the final derived emissions (blue lines). The open circles are the atmospheric observations (Northern Hemisphere – grey and Southern Hemisphere – light blue), with the vertical lines being the associated observational uncertainty. The detection limits for the instruments are shown as the grey shading, with dark grey for the SIO instrument and the light grey for the CSIRO instrument.
Fig. 2. Global annual bottom-up emission estimates from 1971 to 2008 by source from EDGARv4.2 for (a) $\text{C}_4\text{F}_{10}$, (b) $\text{C}_5\text{F}_{12}$, (c) $\text{C}_6\text{F}_{14}$ and (d) $\text{C}_7\text{F}_{16}$. (Note: $\text{C}_8\text{F}_{18}$ is not available from EDGARv4.2.).
Fig. 3. Average absorption cross-section for (a) C\textsubscript{7}F\textsubscript{16} and (b) C\textsubscript{8}F\textsubscript{18} measured at 1 cm\textsuperscript{-1} resolution and 296 K. The spectra were measured over a range of 500–4000 cm\textsuperscript{-1}, although only the main spectral features are shown.
Fig. 4. The global annual emissions for C$_{4}$F$_{10}$, C$_{5}$F$_{12}$, C$_{6}$F$_{14}$, C$_{7}$F$_{16}$ and C$_{8}$F$_{18}$ derived in this study are shown as the solid blue line, and the associated 1-σ uncertainty in the emissions is represented as the light blue shading. The available bottom-up emissions data are also shown from EDGARv4.2 (solid yellow line) and UNFCCC (solid purple line). The interpolated data used in the reference run from EDGARv4.2 from 2009 to 2011 are shown as the dashed blue line, and the C$_{8}$F$_{18}$ reference emissions are also shown as a dashed line, as no bottom-up estimates are available and C$_{7}$F$_{16}$’s emissions were used as a proxy.
Fig. 5. The mole fraction residuals, taken as the observations minus final modeled mole fractions (Northern Hemisphere – grey and Southern Hemisphere – light blue). The vertical lines represent the uncertainty associated with each observation. A zero line is also plotted for reference.
Fig. 6. Global annual PFC emissions in CO₂ equivalents, using GWPs with a 100-yr time horizon, from 1973 to 2009. The CF₄, C₂F₆ and C₃F₈ emissions are from Mühle et al. (2010) and the c–C₄F₈ emissions are from Oram et al. (2012). The bottom panel shows the relative percentage the high molecular weight PFCs studied here contribute to the new global total of PFC emissions in CO₂ equivalents.