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## Global and regional emissions of HFC-125 (CHF<sub>2</sub>CF<sub>3</sub>) from in situ and air archive atmospheric observations at AGAGE and SOGE observatories

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[1] High-frequency, in situ observations from the Advanced Global Atmospheric Gases Experiment (AGAGE) and System for Observation of halogenated Greenhouse gases in Europe (SOGE) networks for the period 1998 to 2008, combined with archive flask measurements dating back to 1978, have been used to capture the rapid growth of HFC-125 (CHF<sub>2</sub>CF<sub>3</sub>) in the atmosphere. HFC-125 is the fifth most abundant HFC, and it currently makes the third largest contribution of the HFCs to atmospheric radiative forcing. At the beginning of 2008 the global average was 5.6 ppt in the lower troposphere and the growth rate was 16% yr<sup>-1</sup>. The extensive observations have been combined with a range of modeling techniques to derive global emission estimates in a top-down approach. It is estimated that 21 kt were emitted globally in 2007, and the emissions are estimated to have increased 15% yr<sup>-1</sup> since 2000. These estimates agree within approximately 20% with values reported to the United Nations Framework Convention on Climate Change (UNFCCC) provided that estimated emissions from East Asia are included. Observations of regionally polluted air masses at individual AGAGE sites have been used to produce emission estimates for Europe (the EU-15 countries), the United States, and Australia. Comparisons between these top-down estimates and bottom-up estimates based on reports by individual countries to the UNFCCC show a range of approximately four in the differences. This process of independent verification of emissions, and an understanding of the differences, is vital for assessing the effectiveness of international treaties, such as the Kyoto Protocol.

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### 1. Introduction

[2] Hydrofluorocarbons (HFCs) were developed as replacements for ozone depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). These partially fluorinated hydrocarbons have effectively zero Ozone Depletion Potentials (ODPs) and therefore are not included

in the Montreal Protocol [*Intergovernmental Panel on Climate Change (IPCC)*, 2006]. There is concern about the accumulation of HFCs in the atmosphere mainly because of their high global warming potential (GWP) and therefore HFC emissions are included in the United Nations Framework Convention on Climate Change (UNFCCC, [http://unfccc.int/national\\_reports/annex\\_i\\_ghg\\_inventories/national\\_inventories\\_submissions/items/3929.php](http://unfccc.int/national_reports/annex_i_ghg_inventories/national_inventories_submissions/items/3929.php)) and the associated

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**Table 1.** Overview of Measurement Stations, the Network to Which They Belong, Their Coordinates, and the Period for Which Data Are Available

Station	Network	Latitude, °N	Longitude, °E	Instrument	Sampling Dates
Mace Head	AGAGE	53.3	-9.9	ADS-GCMS	1998–2004 <sup>a</sup>
Mace Head	AGAGE	53.3	-9.9	Medusa GCMS	June 2003 to present
Trinidad Head	AGAGE	41.0	-124.1	Medusa GCMS	Mar 2005 to present
Ragged Point	AGAGE	13.2	-59.4	Medusa GCMS	May 2005 to present
Cape Matatula	AGAGE	-14.2	-170.6	Medusa GCMS	May 2006 to present
Cape Grim	AGAGE	-40.7	144.7	ADS-GCMS	1998–2004 <sup>a</sup>
Cape Grim	AGAGE	-40.7	144.7	Medusa GCMS	Jan 2004–present
Zeppelin	SOGE	78.9	11.9	ADS-GCMS	2000–2008
Jungfrauoch	SOGE	46.5	8.0	ADS-GCMS	2000 to present <sup>b</sup>

<sup>a</sup>Monitoring of HFC-125 began in 1998.

<sup>b</sup>Medusa GCMS measurements started in spring 2008.

Kyoto Protocol. HFC-125 (CHF<sub>2</sub>CF<sub>3</sub>) has a significant radiative forcing value with a GWP of 3500 integrated over 100 years [Forster *et al.*, 2007]. HFC-125 mol fractions are currently significantly lower than the most abundant CFCs and HCFCs, but have been increasing rapidly [Forster *et al.*, 2007; Clerbaux and Cunnold, 2007]. In 2000–2004 measurements of HFC-125 from Cape Grim, Tasmania and Mace Head, Ireland showed that mole fractions were increasing approximately exponentially at 23% yr<sup>-1</sup>. In mid-2005 the globally averaged value derived from these measurements was 3.7 ppt (parts per 10<sup>12</sup> molar) [Forster *et al.*, 2007]. Countries that have ratified the Kyoto Protocol have committed to reduce their emissions of greenhouse gases. Signatories to the Protocol can use emissions trading to meet their emissions commitments. Global atmospheric observations are an independent and effective method of assessing globally aggregated reductions in emissions of individual greenhouse gases.

[3] HFC-125 is mainly used as a component in refrigerant blends for commercial refrigeration applications (R-402, R-404, R-407, R-408, R-410, R-417, R-507), replacing HCFC-22 (CHClF<sub>2</sub>) [Velders *et al.*, 2009]. HFC-125 also has minor uses as a halon replacement in fire-fighting equipment. As the phase-out of HCFC-22 gains momentum it might be expected that demand for refrigerant blends containing HFC-125 will increase.

[4] HFC-125 is removed from the atmosphere by gas phase reaction with hydroxyl radicals (OH), and the degradation products resulting from this reaction are carbonyl fluoride (COF<sub>2</sub>) and trifluoromethanol (CF<sub>3</sub>OH). The reaction rate with OH has been estimated to be  $6.0 \times 10^{-13} \exp(-1700\text{K}/T) \text{ cm}^3 \text{ s}^{-1}$  [Sander *et al.*, 2006]. The atmospheric lifetime of HFC-125 is estimated to be 29 years [Forster *et al.*, 2007].

## 2. Experimental Methods

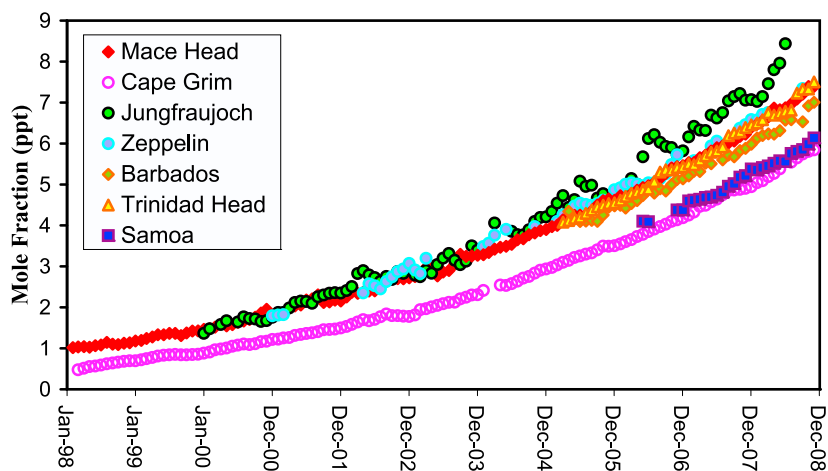
### 2.1. Instrumentation

[5] High-frequency, in situ measurements of HFCs were obtained using automated gas chromatography–mass spectrometry (GC-MS) systems by incorporating the preconcentration and analysis of 2 L air samples. The original GC-MS systems comprised an adsorption-desorption unit (ADS) coupled to a quadrupole GC-MS instrument (Agilent 5973, Berkshire, England) [Simmonds *et al.*, 1995, 1996, 1998]. These systems were installed at two Advanced Global Atmospheric Gases Experiment (AGAGE) stations,

Mace Head, Ireland, and Cape Grim, Tasmania in 1998 and two System for Observation of halogenated Greenhouse gases in Europe (SOGE) sites, Jungfrauoch, Switzerland, and Zeppelin, Spitzbergen, Norway in 2000. The ADS-GC-MS was replaced by a technologically improved preconcentration system: the Medusa GC-MS [Miller *et al.*, 2008]. Medusa systems were installed initially at Mace Head and Cape Grim, followed by phased installation at all other AGAGE stations, Trinidad Head, California, Ragged Point, Barbados and Cape Matatula, American Samoa. Measurements of HFC-125 started in 1998. Table 1 identifies the locations of the contributing stations and instrumentation used to acquire the data.

[6] Analysis of each air sample was alternated with analysis of a reference gas to determine and correct for instrumental drift resulting in 6 (ADS) and 12 (Medusa) fully calibrated air samples per day. Working standards were prepared for each AGAGE station by compressing ambient air into 35 L electropolished stainless steel canisters (Essex Cryogenics, Missouri) using a modified oil-free compressor (SA-3, RIX California). An exception to this was the Cape Grim station, where the working standards were filled using a cryogenic filling technique. Working standards were filled to 40–60 bar and had a working life of approximately 2 months. Such a rapid turnaround of working standards resulted in minimal sampling and detector nonlinearity issues since the ambient mole fractions and working standard mole fractions were very similar. Research-grade helium, which was used as a carrier gas in the system, was analyzed for blanks on a regular basis and blank levels were below the limit of detection at all field stations. HFC-125 was detected with the MS in selected ion monitoring mode (SIM) using a target ion, C<sub>2</sub>F<sub>4</sub>H<sup>+</sup> (*m/z* 101), and qualifier ions CF<sub>2</sub>H<sup>+</sup> (*m/z* 51) and CF<sub>3</sub><sup>+</sup> (*m/z* 69). The ratios of the target ion/qualifier ions were monitored to ensure that potential interferences from coeluting species did not affect the analysis. Instrument precision was determined as one standard deviation of the ratio of each standard response to the average of the closest in time preceding and subsequent standard responses. Typically the precision was 640 ppq (parts per 10<sup>15</sup> molar) or 1.6% for ADS data and 280 ppq or 0.7% for Medusa data.

[7] In order to extend the HFC-125 data record back before the commencement of high-frequency measurements, analysis of Northern and Southern Hemispheric archived air samples was carried out using two identical Medusa GC-MS instruments at the Scripps Institution of



**Figure 1.** Baseline monthly mean HFC-125 mol fractions (ppt) from in situ (ADS and Medusa-GCMS) measurements at AGAGE and SOGE stations.

Oceanography (SIO), La Jolla, California and the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Aspendale, Australia, respectively (B. R. Miller et al., manuscript in preparation, 2009). The Southern Hemisphere (SH) samples are part of the Cape Grim Air Archive (CGAA) [Langenfelds et al., 1996; Krummel et al., 2007]. The Northern Hemisphere (NH) samples used for this paper were filled during background conditions mostly at Trinidad Head, but also at La Jolla, California, Cape Meares, Oregon (courtesy of the Norwegian Institute for Air Research, Oslo, Norway), and Point Barrow, Alaska (courtesy of Robert Rhew, University of California, Berkeley). In addition, six SH samples were measured at SIO, all in good agreement with the SH samples of similar age measured at CSIRO (February 1995, July 1995, September 1995, November 1995, and January 2004,  $\Delta x = 0-0.02$  ppt,  $\Delta t = 9-33$  days) and three NH samples were measured at CSIRO, all in good agreement with NH samples of the same age measured at SIO (May 1989 and April 1999,  $\Delta x = 0.01-0.02$  ppt,  $\Delta t = 0-12$  days). The good agreement for samples from 1989–2004 between SIO and CSIRO stored in different types of tanks (Stainless steel tanks, Essex Cryogenics and Silcosteel treated tanks, Restek Corporation) serves both as proof of the good agreement of the two Medusa systems and the integrity of the used tanks. The archived samples were analyzed in replicate typically 3–6 times each. Several NH tanks were remeasured over a 2–2.5 year period. The standard deviation of the mean is less than the overall precision of 28 ppq. Nonlinearity data were collected before, during and after the analyses period and frequent inclusion of blank runs allowed blank corrections to be applied where needed. The Aspendale Medusa GC-MS showed negligible blanks and linear response over 5% to 200% of the range of the calibration standard used (3.04–0.02 ppt). A small blank was observed in the SIO Medusa GC-MS due to HFC-125 impurity in the used Helium carrier gas. This carrier gas blank was carefully accessed for each carrier gas tank. If the variability of the blank was negligible, all measurements during the lifetime of a particular carrier gas tank were blank corrected, otherwise measurements were rejected. The resulting uncertainty due to the blank level variability was negligible in comparison to the

overall precision of 28 ppq. We did not observe any significant blank levels stemming from the used tanks (Essex Cryogenics) or the pressure regulators (Valin Corporation).

## 2.2. Calibration

[8] Assignment of ambient air measurements to a robust traceable calibration scale is of paramount importance. This is achieved at AGAGE stations using a calibrated ambient air standard to bracket each ambient air measurement. A detailed explanation for the calibration of the ambient air values obtained using the ADS GC-MS is documented by O'Doherty et al. [2004] and Prinn et al. [2000], calibration of the Medusa GC-MS is described by Miller et al. [2008]. Absolute calibration for HFC-125 is reported on the UB-98 scale [O'Doherty et al., 2004] maintained at SIO.

## 3. Results and Discussion

### 3.1. Trends and Seasonal Cycles

[9] Baseline values of HFC-125 (expressed as dry gas mole fractions in ppt) are calculated by removing regional pollution effects using the AGAGE pollution identification algorithm (as in work by Cunnold et al. [2002]). The increases in baseline mole fractions at all the AGAGE and SOGE sites are evident in Figure 1, where each data point represents a baseline monthly average. For example, mole fractions at Mace Head have increased from 1.0 ppt in 1998 to 8.8 ppt by June 2008, Cape Grim increased from 0.5 ppt in 1998 to 5.4 ppt by June 2008.

[10] The monthly means of the baseline values have been fitted with the empirical model shown here:

$$\chi(t) = a + b \left( \frac{N}{12} \right) P_1 \left( \frac{t}{N} - 1 \right) + \frac{1}{3} d \left( \frac{N}{12} \right)^2 P_2 \left( \frac{t}{N} - 1 \right) + c_1 \cos \left( \frac{2\pi t'}{12} \right) + s_1 \sin \left( \frac{2\pi t'}{12} \right) + c_2 \cos \left( \frac{4\pi t'}{12} \right) + s_2 \sin \left( \frac{4\pi t'}{12} \right), \quad (1)$$

where  $a$ ,  $b$ , and  $d$  represent the mean, the linear trend, and a curvature term (the rate of change of the trend), respectively. The average seasonal cycle is represented by

**Table 2.** Empirical Model Coefficients for HFC-125 Observations<sup>a</sup>

Site	$a$ , ppt	$b$ , ppt yr <sup>-1</sup>	$d$ , ppt yr <sup>-2</sup>	$c_1$ , ppt	$s_1$ , ppt	$c_2$ , ppt	$s_2$ , ppt
<i>February 1998 to June 2008</i>							
Mace Head	3.20 ± 0.01	0.55 ± 0.00	0.08 ± 0.00	0.00 ± 0.01	0.01 ± 0.01	0.00 ± 0.01	-0.01 ± 0.01
Cape Grim	2.39 ± 0.01	0.45 ± 0.00	0.06 ± 0.00	0.01 ± 0.01	0.01 ± 0.01	-0.01 ± 0.01	-0.01 ± 0.01
<i>January 2000 to June 2008</i>							
Zeppelin	3.74 ± 0.03	0.64 ± 0.01	0.05 ± 0.01	-0.07 ± 0.03	-0.03 ± 0.03	0.06 ± 0.03	-0.02 ± 0.03
Mace Head	3.66 ± 0.01	0.62 ± 0.01	0.08 ± 0.01	-0.00 ± 0.01	0.01 ± 0.01	-0.01 ± 0.01	-0.02 ± 0.01
Jungfraujoch	3.97 ± 0.03	0.73 ± 0.01	0.11 ± 0.01	0.11 ± 0.04	0.04 ± 0.04	0.02 ± 0.04	-0.01 ± 0.04
Cape Grim	2.76 ± 0.01	0.51 ± 0.00	0.07 ± 0.00	0.02 ± 0.01	0.01 ± 0.01	-0.01 ± 0.01	-0.01 ± 0.01

<sup>a</sup>See equation (1) in section 3.1. Observations are at Mace Head, Ireland, and Cape Grim, Australia, from February 1998 to June 2008 (AGAGE data), and at Zeppelin, Norway, Mace Head, Ireland, Jungfraujoch, Switzerland, and Cape Grim, Tasmania, from January 2000 to June 2008 (AGAGE and SOGE data) with one sigma uncertainties. Abbreviations:  $a$  is the mean,  $b$  is the trend,  $d$  is the rate of change of the trend,  $c_1$  and  $s_1$  are annual cycle coefficients, and  $c_2$  and  $s_2$  are semiannual cycle coefficients. Time zero for the seasonal terms is July 1.

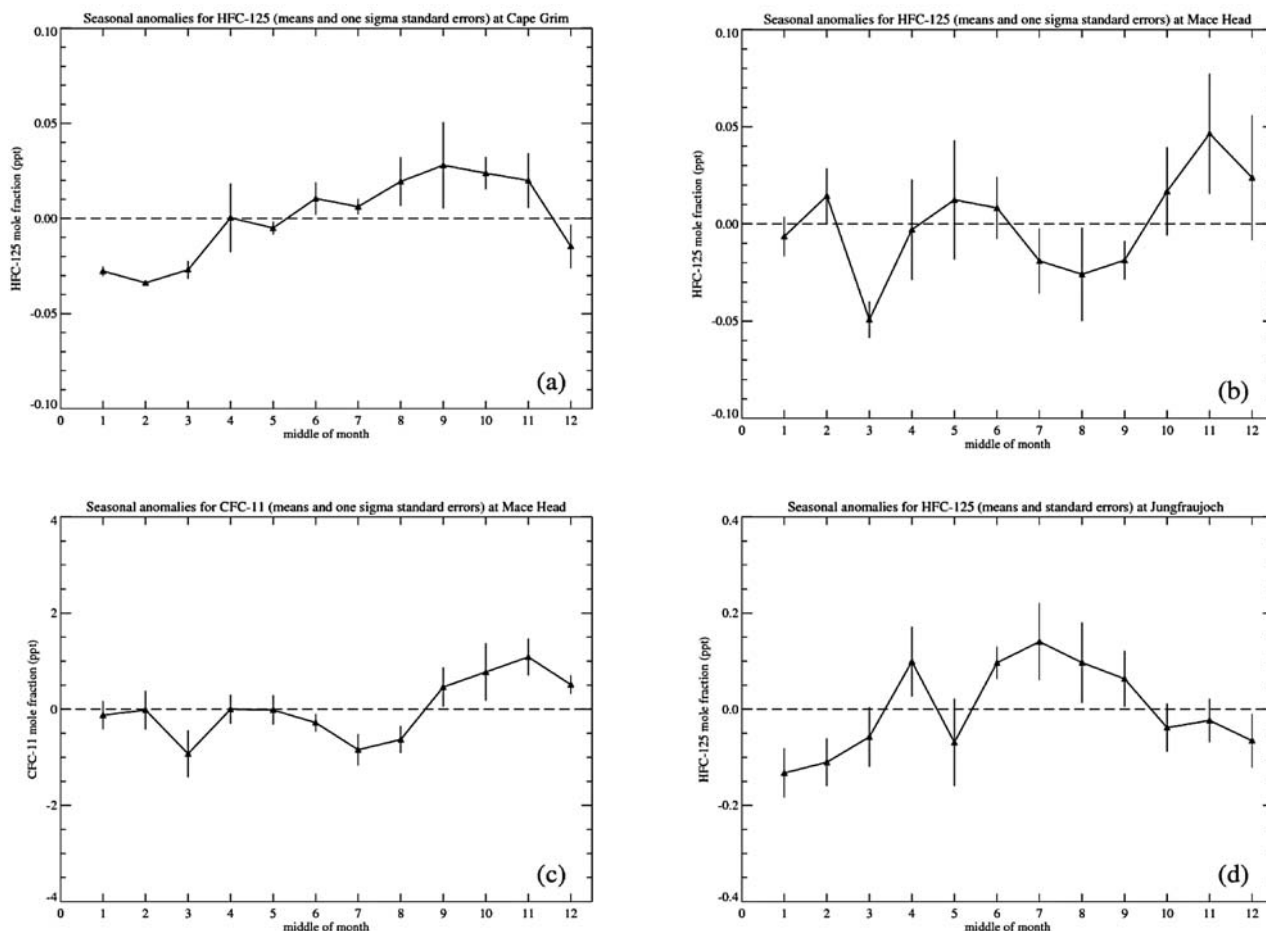
an annual ( $c_1$  and  $s_1$ ) cycle and a semiannual ( $c_2$  and  $s_2$ ) cycle. Time is measured in months: time  $t'$  is zero for the annual cycle terms on 1 July, whereas time  $t$  is measured from the first day used in the analysis determining the  $a$ ,  $b$ , and  $d$  terms;  $N$  is the value of  $t$  at the midpoint of the period being analyzed. The  $P_i$  are Legendre polynomials of order  $i$ , which are used to ensure approximate orthogonality between the estimated coefficients.

[11] The coefficients for Mace Head and Cape Grim from February 1998 to June 2008 are shown in Table 2. The uncertainties given for the coefficients are based on smoothed spectra of the residuals [Cunnold *et al.*, 1994]. SOGE measurements of HFC-125 started later, at Jungfraujoch in January 2000 and at Zeppelin, with a few gaps, in early 2000. Because the accumulation rate of HFC-125 in the atmosphere is changing fairly rapidly, comparisons between the empirical model coefficients are most meaningful for similar periods. Therefore the coefficients for the SOGE sites are compared to those for the AGAGE sites from January 2000 to June 2008.

[12] The results indicate rapid growth of HFC-125 in the atmosphere and the rate of growth (ppt yr<sup>-2</sup>) has been increasing, as is indicated by positive values of  $d$ . The globally averaged mole fraction in the lower troposphere at the beginning of 2008 is estimated to be 5.6 ppt, and the rate of increase in 2007 was 0.8 ppt yr<sup>-1</sup> (16% yr<sup>-1</sup>). The empirical model calculations were repeated using the natural logs ( $\ln$ ) of the mole fractions, which yielded negative values of the coefficient  $d$  (% yr<sup>-2</sup>), but after conversion of the coefficients back to mole fractions, the residuals of the empirical model representations were found to be very similar. This indicates that the growth of HFC-125 in the atmosphere since 1998 has been approximately intermediate between linear and exponential growth. The mean for the Jungfraujoch measurements is approximately 8% higher than the Mace Head mean and is 13% higher in 2008. This is mostly because of generally higher summer values at Jungfraujoch as well as even higher measurements in all seasons in 2007 and 2008. The trend and curvature terms are also significantly larger at Jungfraujoch which is consistent with increasing differences between Jungfraujoch and Mace Head, both in ppt and percentage. The mean mole fraction at Zeppelin is just 2% higher than the mean at Mace Head and the Zeppelin trend is closer to that at Mace Head than to that at Jungfraujoch. A possible explanation for the higher accumulation of HFC-125 at Jungfraujoch is discussed below in terms of the seasonality of the boundary layer height at Jungfraujoch.

[13] The seasonal cycle terms derived from empirical model fit typically do not differ from zero by much more than the one sigma level of confidence (Table 2). Nevertheless the broad-scale features of the calculated seasonal cycles are consistent with the seasonal cycles in many other gases measured by AGAGE at Mace Head and Cape Grim. The reason the seasonal cycle terms in Table 2 show less significant is mainly due to the difficulty of the ADS instrument to detect such small-scale variability. The typical precision of ADS in HFC-125 is 0.6 ppt. It is improved to ~0.3 ppt when the ADS instruments at Mace Head and Cape Grim were replaced by Medusa in 2004. The seasonal cycle of HFC-125 can be better illustrated by using data measured by Medusa (e.g., Figures 2a and 2b). The observed seasonal cycle at Cape Grim exhibits a broad maximum (June–November) centered in NH late winter and a minimum in February (Figure 2a). This behavior is seen in many of the other halogenated compounds measured by AGAGE [O'Doherty *et al.*, 2004]. The AGAGE 2-D 12 box model [Cunnold *et al.*, 1994] approximately simulates the phase and amplitude, and predicts that transport and OH effects contribute approximately in phase to this cycle at Cape Grim. Using a reaction rate of  $6.0 \times 10^{-13} \exp(-1700\text{K}/T) \text{ cm}^3 \text{ s}^{-1}$  [Sander *et al.*, 2006] and OH concentrations from Prinn *et al.* [2005] the tropospheric lifetime of HFC-125 is calculated to be approximately 28 years. Because the lifetime is much longer than the time scale of interhemispheric exchange (~1 year) the in situ OH sink is calculated to drive only between one third and one quarter of the observed annual cycle in HFC-125 at Cape Grim.

[14] In the NH the empirical model calculations (equation 1) show similar results to the observations, which suggest a late fall maximum at Mace Head (Figure 2b) and a late spring/early summer maximum at Jungfraujoch (Figure 2d). Note that the Zeppelin seasonal cycles are not discussed here due to the discontinuity of the measurement record and large error bars. The seasonal variations are illustrated by examining the individual averages for each month after subtraction of running 12 month means. For Mace Head (Figure 2b) both the Medusa alone and the combined Medusa/ADS time series exhibit a fall (November) maximum. We show only the Medusa result (Figure 2b) primarily because they have higher precision than the earlier ADS measurements. A fall maximum is observed for many other species which have seasonal cycles primarily controlled by transport. CFC-11 (CCl<sub>3</sub>F), not removed by OH, shown in Figure 2c, for example, has a remarkably similar seasonal



**Figure 2.** Seasonal cycles derived from means and standard errors of the baseline means for each month of the year obtained after subtraction of the 12 month centered moving averages. (a) Medusa HFC-125 measurements at Cape Grim from February 2004 to June 2008, (b) Medusa HFC-125 measurements at Mace Head from January 2004 to June 2008, (c) CFC-11 measurements at Mace Head from February 1987 to December 1993, and (d) HFC-125 measurements at Jungfraujoch from January 2000 to June 2006.

cycle to that of HFC-125 except that the summer minimum is delayed into September for HFC-125 because of losses due to OH. The period for the CFC-11 seasonal variation calculation was chosen to be from 1987 to 1993 because the locations of CFC-11 emissions were then roughly similar to those for HFC-125. The observed cycle may also be compared with those of HFC-134a and several HCFCs at Mace Head [O'Doherty *et al.*, 2004]. All these gases show a fall maximum as well as below average values in August. In addition the magnitude of the fall maxima (in November) are approximately proportional to the latitudinal gradients estimated from Mace Head/Cape Grim annual mean differences. This is consistent with the fall maxima at Mace Head being produced by transport effects.

[15] Jungfraujoch (Figure 2d) exhibits a different seasonal cycle from that at Mace Head with a maximum in the summer months. The observed higher background concentration in summer is strongly influenced by the enhanced exchange with the more polluted European boundary layer. This is caused by the higher-energy contents of the warmer air masses in summer, by which average vertical mixing along the Alpine ridge (i.e., mountain venting) from the

surrounding boundary layer is enhanced [Henne *et al.*, 2005]. This results in Jungfraujoch mole fractions to be similar to those observed at other remote NH sites except for summer. This effect is also illustrated in the latitudinal gradient of the measured HFC-125 values as shown in Table 3, which includes AGAGE measurements from Trinidad Head, Ragged Point, Cape Matatula, as well as SOGE measurements from Zeppelin and (excluding Jungfraujoch) shows a clear north-south gradient in HFC-125. Table 3 also shows that calculated means from the AGAGE 2-D 12 box model (based on HFC-125 global emissions determined from the AGAGE measurements) are in excellent agreement with the annual means measured at the AGAGE sites. This means that the CFC-11, CFC-12 (CCl<sub>2</sub>F<sub>2</sub>) based transport coefficients are producing good simulations for HFC-125 as well.

### 3.2. Emission Estimates

#### 3.2.1. Emissions Calculated From Country Data, Independent of Atmospheric Measurements

[16] There are two principal sources of information on production and emissions of HFC-125; neither of which, on its own, provides a complete and accurate database of global emissions.

**Table 3.** Comparison Between Measured HFC-125 Annual Mean Mole Fractions and AGAGE 2-D 12 Box Model Results for July 2006 to June 2007<sup>a</sup>

Site	Latitude, °N	Measured 12 Month Mean, ppt	Mean From Box Model, ppt
Zeppelin (S)	78	6.48 ± 0.07	
Mace Head (A)	53	6.34 ± 0.04	6.34
Jungfraujoch (S)	46	7.19 ± 0.12	
Trinidad Head (A)	41	6.38 ± 0.04	6.34
Ragged Point (A)	13	5.94 ± 0.06	5.98
Cape Matatula (A)	-14	5.22 ± 0.03	5.20
Cape Grim (A)	-41	4.98 ± 0.03	5.01

<sup>a</sup>The interannually constant model transport coefficients were tuned to match the observed average gradient of CFC-11 and CFC-12 from 1979 to 1995; over that period most of the sources of those gases were in the United States and Europe. AGAGE sites are indicated by (A), and SOGE sites are indicated by (S).

[17] The more geographically comprehensive source of information is provided by the parties to the Rio Convention (United Nations Framework Convention on Climate Change), available on <http://unfccc.int>. Countries consuming HFCs currently report annual national emission inventories recalculated as apparently homogeneous databases each year; historical values are not fixed but can change in the recalculation. The data used here were recalculated in 2008 and cover the years 1990 to 2006. Although these data are comprehensive, they were compiled using a range of methods, furthermore the total reported emissions of HFC-125 are insufficient to match observed atmospheric mole fractions [McCulloch, 2008]. Underreporting of emissions is a common problem when estimates are based on estimates of equipment numbers and standard rates of emission [IPCC, 2006]. Furthermore, there is a wide range of allowable “standard” rates of emission that result in countries with similar economies and demand patterns having widely differing reported emission rates [McCulloch, 2009].

[18] The sales and emissions survey of HFCs in the European Union conducted by Cefic from 1990 to 2006, and now subsumed into the data collection required by European law [European Community, 2006], gathers audited data for the EU from chemical producers. From these data, emissions can be calculated using well-established emission functions [McCulloch *et al.*, 2003].

[19] Applied to global sales of HFC-134a, these functions provide emissions that match well with global atmospheric mole fractions [Ashford *et al.*, 2004] and this approach was used to reconstruct a global database of HFC-125 emissions based on the production quoted in the UNFCCC data. Where national emissions were quoted as the total HFC release in tonnes of CO<sub>2</sub> equivalent (wholly for the United Kingdom and partially by Austria, Finland, Luxembourg and Netherlands) the HFC-125 component was calculated using the average GWP-weighted fraction within the rest of the EU. Emissions from non-EU countries that did not quote production data were increased by the annual factors calculated from EU data. For those countries that published production data (for example, United States) emissions were calculated directly using the global emission functions. The methods used are described in greater detail in Appendix A.

[20] In addition to the emissions from the use of HFC-125, there are smaller emissions thought to be by-products

from the manufacture of fluoropolymer intermediates. For example, HFC-125 is formed when HCFC-22 is pyrolyzed. This occurs either by the addition of hydrogen fluoride (HF) to tetrafluoroethene (C<sub>2</sub>F<sub>4</sub>) or by insertion of difluorocarbene (CF<sub>2</sub>) into trifluoromethane (HFC-23, CHF<sub>3</sub>) [Hauptschein and Fainberg, 1961]. To calculate these potential emissions it was assumed that all of the byproduct sources would equal the amount of HFC-125 produced by 0.4% of HFC-23 in the global quantity of HCFC-22 used to make C<sub>2</sub>F<sub>4</sub> [from Velders and Madronich, 2005].

[21] Global and regional emissions based on the reanalysis of country data and historical by-products are shown in Tables 4, 5, 6, and 7 and hereafter referred to as McCulloch derived emissions (a full description of the methodology used to derive these emissions can be found in Appendix A). The global totals of emissions have relatively low uncertainty, estimated to be better than ±20% [McCulloch *et al.*, 2003]. In view of the wide difference in calculation methods, the distribution between countries is much less certain and impossible to quantify.

### 3.2.2. Global Emissions of HFC-125 Inferred From Atmospheric Measurements

[22] Global emissions of HFC-125 are estimated from an inversion of the annual means of the measurements [Cunnold *et al.*, 1994; Prinn *et al.*, 2000] using the AGAGE 2-D 12 box model [Cunnold *et al.*, 1983, 1994] as the forward model. This model consists of four equal mass, semihemispheric lower tropospheric boxes (1000–500 hPa), four equal mass upper tropospheric boxes (500–200 hPa), and four equal mass stratospheric boxes from (200–0 hPa) with a troposphere/stratosphere exchange time of 2 years. The model has transport coefficients which have been tuned to represent CFC-11 and CFC-12 measurements prior to the early 1990s when the global distribution of the emissions was relatively well known [Cunnold *et al.*, 1994]. The model uses an equilibrium lifetime for HFC-125 within the stratosphere of 38 years; this is based on a stratospheric

**Table 4.** Estimates of Global Emissions of HFC-125 Based on AGAGE in Situ Measurements and Archived Air Samples Collected Since 1978, Primarily at Trinidad Head and Cape Grim, Using the AGAGE 2-D 12 Box Model<sup>a</sup>

	AGAGE	UNFCCC	McCulloch	EDGAR
Total < 1978			0.6	
Total < 1984			0.9	
Total < 1994	2.0 ± 2.0		2.4	
1994	1.3 ± 0.3	0.1	1.0	0.7
1995	2.1 ± 0.4	0.5	1.6	1.2
1996	2.8 ± 0.5	0.9	2.5	1.6
1997	4.6 ± 0.8	1.5	3.5	2.1
1998	6.1 ± 1.1	2.0	4.6	
1999	5.7 ± 1.3	2.6	5.6	
2000	7.5 ± 1.7	3.3	6.7	8.7
2001	8.8 ± 2.8	4.1	7.9	
2002	10.6 ± 2.5	4.8	9.4	
2003	11.9 ± 3.3	5.7	11.0	
2004	13.5 ± 3.6	6.7	12.7	
2005	15.8 ± 3.3	7.7	13.7	
2006	18.2 ± 3.9	8.8		
2007	20.5 ± 4.3			

<sup>a</sup>Unit is kt yr<sup>-1</sup>. Estimates of total emissions prior to 1998 are based only on archived air samples. Also shown are global emission estimates derived from UNFCCC (2008 submission), McCulloch, the EDGAR database, and Campbell and Shende [2005].

**Table 5.** Annual Estimates of Emissions of HFC-125 From the EU-15 Region<sup>a</sup>

Year	AGAGE <sup>b</sup>	UNFCCC	McCulloch	NAME
1994		0.1	0.1	
1995		0.2	0.2	
1996		0.2	0.3	
1997		0.4	0.6	
1998	1.6 (1.4–1.9)	0.6	0.9	
1999	2.1 (1.7–2.4)	0.8	1.3	1.3 (0.9–2.0)
2000	2.1 (1.8–2.4)	1.0	1.8	1.6 (0.9–3.2)
2001	2.5 (2.0–2.9)	1.4	2.4	2.3 (1.0–3.5)
2002	2.0 (1.8–2.2)	1.6	3.1	2.8 (2.0–3.6)
2003	2.2 (1.7–2.8)	2.1	3.8	2.9 (2.0–4.2)
2004	3.5 (3.1–3.9)	2.4	4.7	3.3 (2.1–5.2)
2005	3.6 (3.0–4.1)	2.8	4.7	3.7 (2.3–5.4)
2006	3.8 (3.1–4.5)	3.2		4.7 (2.8–9.0)
2007	3.7 (3.0–4.5)			5.5 (3.6–9.0)

<sup>a</sup>Based on AGAGE in situ measurements using the interspecies correlation method with CO, UNFCCC data (2008 submission), modified UNFCCC data (McCulloch), and the NAME model. Unit is kt yr<sup>-1</sup>.

<sup>b</sup>Based on a CO interspecies correlation technique (see text).

loss contribution to the global lifetime of HFC-125 of 246 years calculated by *Naik et al.* [2000]. This combined with the *Prinn et al.* [2005] OH concentrations and semi-hemispheric proportions of the emission percentages of 84.1:12.4:1.2:2.3 from north to south result in a global equilibrium lifetime for HFC-125 of 28 years.

[23] The emission distribution is based on the methodology of *McCulloch et al.* [2003] and it is similar to that for HFC-134a except within the SH. It should be noted however that the global emission estimates are relatively insensitive to uncertainties in these emission percentages because the global emission estimates are approximately dependent on the annual changes in the global averages of the measurements. Because the model does not simulate the amplitude of the seasonal cycles well at all the measurement sites (especially at Barbados), annual means instead of monthly values are used in the calculations. SOGE measurements at Jungfrauoch have not been included in the inversion because, as indicated in Tables 2 and 3, and discussion in section 3.1, the baseline measurements there are indicated to be strongly influenced by regional factors.

[24] The inversion procedure used in the calculations is similar to that described for example by *Prinn et al.* [2000]. It uses recursive estimation [*Chen and Prinn*, 2006] with annual pulses and 100% a priori uncertainties for each year of emissions. The inversion produces emissions that result in calculated annual mean mole fractions which simulate the averages of the Mace Head and Cape Grim measurements typically within 0.02 ppt. The emission estimates are based on OH concentrations from *Prinn et al.* [2005] that varied from year to year. However, because of the small loss rate for HFC-125 the differences between these estimates and those using an averaged OH are approximately  $\pm 0.1$  kt yr<sup>-1</sup>, which is not significant.

[25] Figure 3 shows a comparison of the continuous AGAGE measurements at Cape Grim and Mace Head and analyses of archived air measurements from Cape Grim and from archived NH air samples. The archived air analyses were made on two Medusa instruments (as described in section 2.1), which provide more precise measurements than the ADS instruments. Based on the archived air

comparisons, the first 18 months of ADS measurements appear to be slightly elevated ( $\sim 0.1$  ppt). Annual emissions prior to 1999 are calculated from the archived measurements alone. From 1999 to 2004 the reported emission estimates are derived from an average of the estimates obtained from the archived air measurements and the in situ AGAGE-ADS and AGAGE-Medusa measurements. From 2005 onward the emission estimates are calculated from just the in situ AGAGE-Medusa measurements at all sites. Figure 3 illustrates the model results using these emission estimates. The dashed lines show the model values for the northernmost and southernmost semihemispheric boxes. The precisions on the measurement based emission estimates are based on the residual differences between the model calculations and the measurements, in addition to measurement uncertainties. Systematic uncertainties in the estimates arise from the reaction rate with OH (approximately 20% from *Sander et al.* [2006]) and the uncertainty in the overall mean OH concentration (14% based on work by *Prinn et al.* [2001]). These uncertainties add a monotonically increasing uncertainty of 0.7 kt yr<sup>-1</sup> in 1999 to 1.2 kt yr<sup>-1</sup> in 2006. An additional source of uncertainty is absolute calibration, estimated to be 5–6%. These systematic uncertainties are not included in the error bars but they would contribute relatively little to the uncertainties shown in Figure 4 because of the long atmospheric lifetime and the rapid atmospheric increase rate of HFC-125.

[26] Table 4 and Figure 4 show a comparison of the global annual emission estimates derived from AGAGE measurements and a number of other sources, such as bottom-up estimates based on McCulloch's reanalysis of country data and historical by-products, emissions reported to UNFCCC, and emissions estimated in the EDGAR database (<http://www.mnp.nl/edgar>). Emissions from the EDGAR database contain historical data from 1990 to 1997 and 2000, and rely on calculations described by *Olivier* [2002] and *Olivier and Berdowski* [2001]. The AGAGE derived global emissions are calculated to have been increasing approximately 15% yr<sup>-1</sup> since 2000 and were around 21 kt yr<sup>-1</sup> in 2007. There is relatively good agreement with McCulloch estimates based on reanalysis of

**Table 6.** Annual Estimates of Emissions of HFC-125 From the United States<sup>a</sup>

Year	UNFCCC 2007	UNFCCC 2008	McCulloch	NAME
1992	0.2		0.2	
1993	0.5	0.01	0.5	
1994	0.7	0.04	0.8	
1995	1.3	0.3	1.3	
1996	1.8	0.6	1.9	
1997	2.5	0.9	2.5	
1998	3.1	1.2	3.1	
1999	3.5	1.5	3.6	
2000	4.0	1.9	4.0	
2001	4.4	2.2	4.4	
2002	4.9	2.4	5.1	
2003	5.5	2.8	5.7	
2004	6.2	3.2	6.5	
2005	7.1	3.7	7.5	
2006		4.4		1.8 (1.0–3.0)
2007				

<sup>a</sup>Based on UNFCCC data (2007 and 2008 submissions), McCulloch, and the NAME model. Unit is kt yr<sup>-1</sup>.



**Table 7.** Annual Estimates of Emissions of HFC-125 From Australia<sup>a</sup>

Year	AGAGE <sup>b</sup>	McCulloch	UNFCCC	DEWHA 2008	Energy Strategies 2008	NAME
1995		0.01	0.004			
1996		0.03	0.01			
1997		0.05	0.02			
1998	0.07 (0.04–0.08)	0.07	0.04			
1999	0.04 (0.02–0.05)	0.10	0.05			
2000	0.04 (0.03–0.06)	0.14	0.08			
2001	0.06 (0.04–0.08)	0.19	0.10			
2002	0.07 (0.05–0.09)	0.24	0.13			
2003	0.10 (0.05–0.13)	0.30	0.17			0.33 (0.23–0.44)
2004	0.13 (0.08–0.18)	0.34	0.20			0.34 (0.23–0.45)
2005	0.13 (0.10–0.17)	0.42	0.23			0.34 (0.34–0.45)
2006	0.08 (0.06–0.11)		0.26	0.25	0.24	0.35 (0.25–0.48)
2007	0.10 (0.06–0.14)					0.37 (0.27–0.48)

<sup>a</sup>Based on AGAGE in situ measurements and using the interspecies correlation method with CO (CSIRO), UNFCCC data (2008 submission), the NAME model, McCulloch, *DEWHA* [2008], and *Energy Strategies* [2008]. Unit is kt yr<sup>-1</sup>.

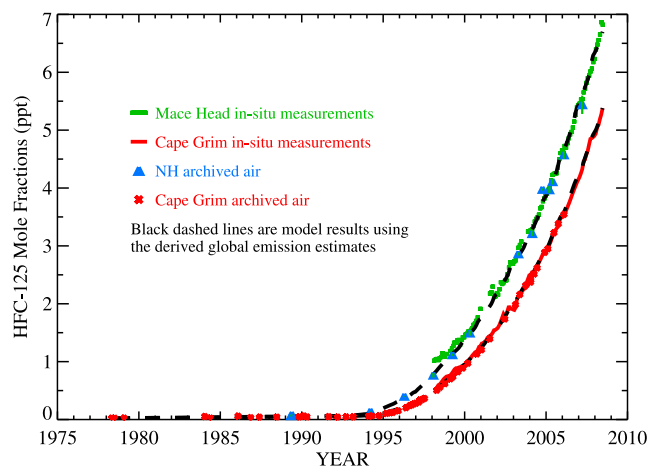
<sup>b</sup>Based on a CO interspecies correlation technique [Dunse *et al.*, 2005].

national emissions reported to the UNFCCC (as described in section 3.2.1, including an allowance for additional emissions in East Asia not reported in the UNFCCC database). In contrast the AGAGE derived emissions are larger than the sum of the national emissions reported to the UNFCCC (2008 submission) by 9.4 kt in 2006. Notably, the UNFCCC database does not contain HFC emission estimates from developing countries in Asia (China, Indonesia, Korea, Malaysia, Philippines, Taiwan, Vietnam etc), from the subcontinent (India, Pakistan, etc.), from the Middle East, from Africa and from Latin America. Global HFC-125 emissions have been reported in IPCC/TEAP for 1995, 2000 and 2002. These historical emissions arise from the use of HFC-125, as derived from production and sales data and sector-specific emission factors [Campbell and Shende, 2005], these data are also shown in Figure 4 alongside estimates based on EDGAR emission data. The estimated emissions from EDGAR agree well with AGAGE calculated emissions in 1994 but appear to grow at a slower rate in subsequent years, whereas the Campbell and Shende derived estimates agree well in 2002 but are low compared to AGAGE estimates in 1995 and 2000. Global AFEAS emission data (not shown) were also reported in the IPCC/TEAP report [Velders and Madronich, 2005] however these values were very low (about 2 kt in 2002) compared to emissions derived from AGAGE data (10.6 kt) and they have subsequently been removed from the AFEAS website pending recalculation (<http://www.afeas.org>).

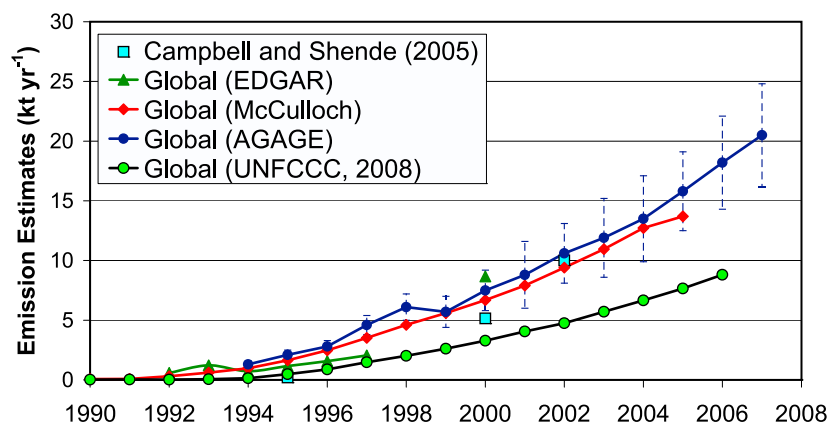
### 3.2.3. Regional Emissions of HFC-125 Inferred for Europe, United States, and Australia

[27] AGAGE measurements have been used to infer emissions for Europe, United States, and Australia by two methods where possible. An interspecies correlation method using carbon monoxide (CO) has been applied to the Mace Head and Cape Grim measurements only to derive emissions for Europe and Australia [Reimann *et al.*, 2005; Dunse *et al.*, 2005]. For Europe this method uses enhancements above baseline values during pollution events identified by the AGAGE pollution identification algorithm and calculates the ratio of the sum of enhancements during a calendar year of HFC-125 to CO for all HFC-125 pollution events. The annual ratios are then multiplied by the annual CO emissions reported, in the case of the European Community (EU-15: Ireland, UK, France, Spain, Portugal, Germany,

Italy, Belgium, the Netherlands, Luxembourg, Denmark, Greece, Austria, Sweden, Finland), CO emissions are taken from Vestreng *et al.* [2004]. Uncertainties in these HFC-125 emission estimates are the standard errors of the means of twelve monthly estimates. For Australia, where SE Australian CO emissions are known, measurements of CO are related to that of other species for which emissions are unknown [Dunse *et al.*, 2005]. A range of pollution markers (CFC-12, CH<sub>2</sub>Cl<sub>2</sub> and HFC-134a), were used to identify episodes caused by SE Australian emissions. Data for these pollution episodes were extracted and correlations between the trace species, in this case HFC-125, in the polluted air masses were calculated. These correlations, were multiplied by an estimate of CO emissions from the SE Australian region, and used to deduce SE Australian emissions of HFC-125. The emission estimates are based on time-dependent annual CO emissions for SE Australia as



**Figure 3.** Archived air sample measurements (mostly from Trinidad Head and La Jolla) from the Northern Hemisphere (blue triangles) and Cape Grim (red crosses) and in situ measurements from Mace Head (green pluses) and Cape Grim (solid red line). The dashed black lines show the excellent fit of the lower tropospheric northernmost and southernmost semihemispheric boxes' mole fractions calculated using the AGAGE 2-D 12 box model with the global emissions having been determined from the observations.



**Figure 4.** Estimates of global emissions of HFC-125 ( $\text{kt yr}^{-1}$ ) based on AGAGE in situ measurements and archived air samples collected since 1978 primarily at Trinidad Head and Cape Grim using the AGAGE 2-D 12 box model. Estimates of total emissions prior to 1994 are quite uncertain because a substantial proportion of the archived air samples prior to that time show mole fractions of zero. Also shown are global emission estimates derived from a range of inventory based data: UNFCCC (2008 submission), McCulloch, the EDGAR database, and *Campbell and Shende* [2005].

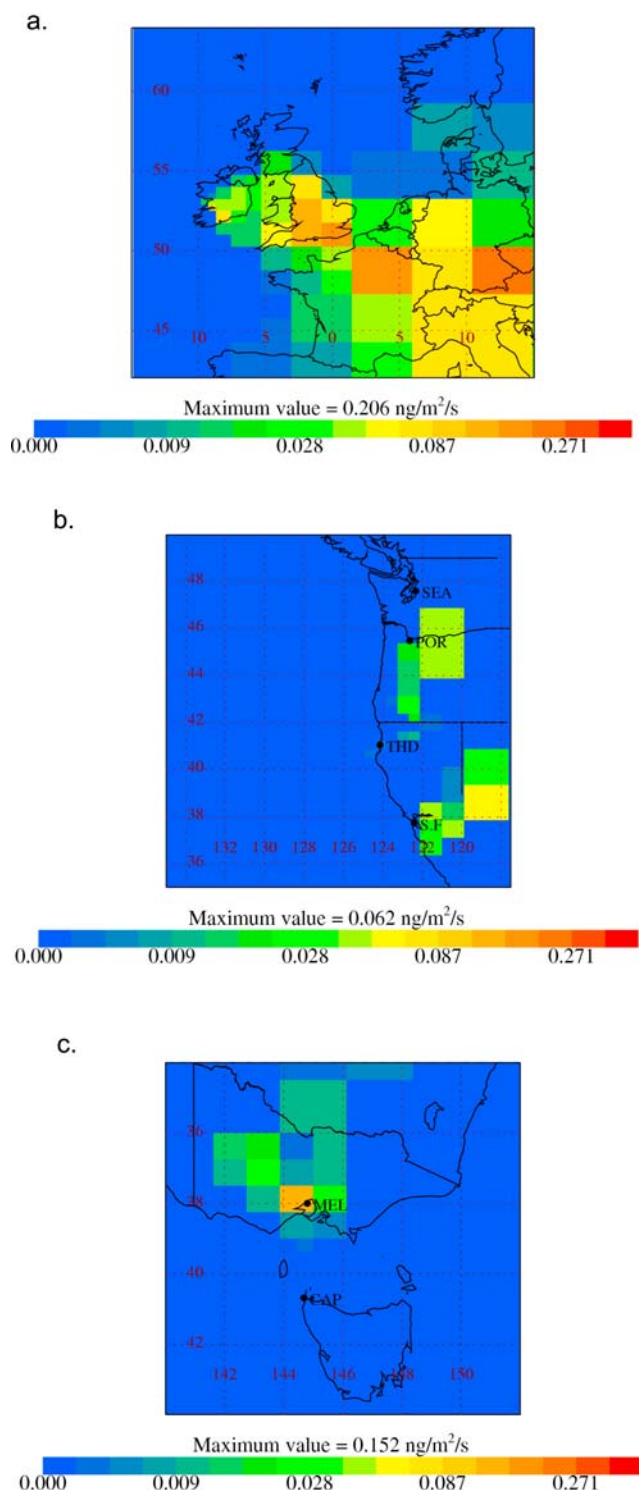
reported for Australia from the Australian government National Pollutant Inventory (NPI) (Australian Government, Department of the Environment, Water, Heritage and the Arts, <http://www.npi.gov.au>). The emission estimates from the SE Australian region are scaled to Australian emissions on a population basis. This type of technique has been used in the past for several other AGAGE species [Reimann *et al.*, 2005] and, although the exact methodology used varies slightly, it has been found to produce emission estimates within a factor of 2 of those from the inverse method based on back trajectories [Manning *et al.*, 2003].

[28] The second method uses the Numerical Atmospheric dispersion Modeling Environment (NAME) [Ryall and Maryon, 1998, Jones *et al.*, 2004] which is a Lagrangian model used in the UK for a wide range of atmospheric dispersion applications such as emergency response [Witham *et al.*, 2007; Webster *et al.*, 2006], estimation of emissions [Derwent *et al.*, 2007; Greally *et al.*, 2007; Simmonds *et al.*, 2004, 2005, 2006; Reimann *et al.*, 2005; O'Doherty *et al.*, 2004; Manning *et al.*, 2003] and air quality studies [Athanasiadou *et al.*, 2006; Redington and Derwent, 2002]. For each 3 h period at Mace Head (1998–2007), Cape Grim and (2003–2007) and Trinidad Head (2005–2007), the NAME model has been used to estimate the recent (10 day) history of the air arriving at the observing station. The 3 h air history maps are used to classify the air masses and have been used to estimate the baseline mole fractions of HFC-125 at each station. The baseline category defines those times when the air has predominately come straight from an ocean sector. Times when the air is slow moving and not well mixed over the observing station are classified as local and are excluded from the baseline category and subsequent emission estimates. This procedure for estimating the baselines is more scientifically rigorous than the AGAGE statistical approach, but in practice the two sets of baselines are quite similar [O'Doherty *et al.*, 2001].

[29] The NAME air history maps provide information on how much HFC-125 is transported from each area within a regional domain (e.g., for Mace Head this is  $21^{\circ}\text{W}$ – $33^{\circ}\text{E}$

longitude by  $35^{\circ}\text{N}$ – $71^{\circ}\text{N}$  latitude) to the observing site; that is, it estimates the dilution of HFC-125 emitted from a particular area to the observation site for each three hour period. The observed mole fraction is a combination of the baseline value and the impact of regional emissions. The deviation of the observations from the baseline mole fractions is an indication of the strength of the regional emissions upwind of the observation. By applying the inversion method as discussed by Manning *et al.* [2003] the regional emissions of any trace gas can be estimated. Figures 5a–5c show the distribution of the estimated emissions of HFC-125 in 2006 for the regional area surrounding each station. The NAME-inversion method has been used to estimate emissions over each 3 year period with monthly intervals, for example, February 1998 to January 2001, March 1998 to February 2001, and so forth. To account for uncertainty a random noise element is added to the observations and multiple solutions are found (eight) for each time interval. The noise has a mean of zero and a standard deviation of four times the standard deviation of the difference between those observations classed as baseline and the smoothed baseline estimates. Annual estimates are derived by averaging all of the 3 year periods that completely overlap the year in question. The minimum and maximum estimates from same solutions are used to derive the upper and lower bounds.

[30] The HFC-125 pollution episodes recorded at Mace Head, Ireland, are largely due to HFC-125 emissions from Western Europe, where there are significant urban source regions. The magnitude of the emissions is population based with high levels from the areas surrounding London, Paris and Munich. Figure 6 and Table 5 show a comparison of HFC-125 emissions for Europe (EU-15 countries). The NAME estimates are calculated for 8 countries (Ireland, UK, France, Germany, Denmark, Belgium, the Netherlands, Luxembourg) and scaled to EU-15 using population. The eight countries represent 63% of the population in the EU-15 (2000 census, <http://www.demographia.com>). The agreement between the various emission estimates for Europe is reasonable (within a factor of 2 after 2001). The AGAGE



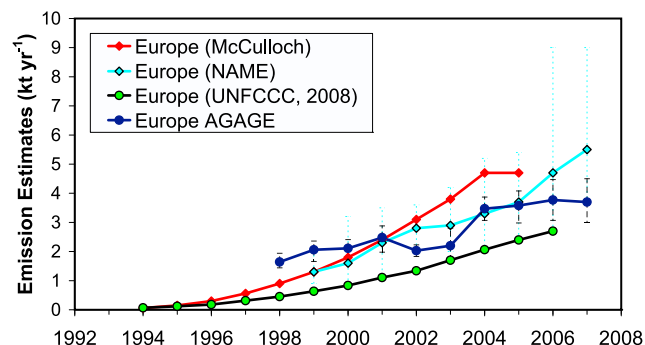
**Figure 5.** NAME-inversion emission distribution and magnitude around each observation station for 2006. (a) Mace Head-northwest Europe, (b) Trinidad Head-west United States, and (c) Cape Grim-southeast Australia.

estimates show a smaller average rate of growth than the NAME, UNFCCC and McCulloch derived values. The measurement based estimates using the CO correlation method give some indication of higher emissions in Europe than expected from inventories before 2000, although the

NAME model estimates are similar to the McCulloch inventory based estimates at that time. More definitively the measurement based estimates are higher than the UNFCCC estimates in every year.

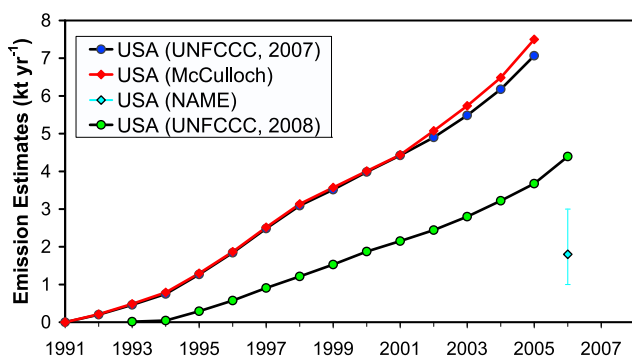
[31] The NAME annual estimates for the United States have only been calculated for the period of 2005–2007 based on measurements from the AGAGE site at Trinidad Head. The U.S. emissions have been calculated by scaling up by population the estimated emissions from an area covering the northwest United States, i.e., northern California, Washington, west Oregon, and west Nevada. This covers a total population of 21.3 million people (estimated from 1990 gridded population distribution (Y. F. Li, Gridded global population distribution for 1990 with 1X1 latitude/longitude resolution, 2006, available from Environment Canada at <http://na.unep.net/metadata/unep/GRID/GLPOP90.html>), scaled to 2005 census totals), 16% of the population of the United States. This method assumes that the emissions of HFC-125 from this 16% of the U.S. population are representative of the per capita emissions for the entire United States. The estimates are shown in Figure 7 and Table 6. The uncertainties in the NAME estimates are significant and relate to the difficulty of using the Trinidad Head data due to the local topography and frequent local flow regimes. These results are significantly lower than the UNFCCC and McCulloch bottom-up estimates. The UNFCCC 2007 submission and McCulloch derived estimates, based on the UNFCCC 2007 submission, shown in Figure 7 agree well prior to 2002, and diverge subsequently in the recalculation of the UNFCCC database. The submission of data to the UNFCCC in 2008 shows a dramatic reduction in estimated emissions, 43% reduction in 2006. The reasoning behind such a dramatic reduction in reported emissions is unclear, but is likely contained in the U.S. EPA documents that form the basis of the U.S. submission to the UNFCCC.

[32] Figure 8 and Table 7 shows a comparison of the emission estimates for Australia. A range of approximately a factor of four in the results is reported. Australian emissions of HFC-125 derived from Cape Grim AGAGE measurements by interspecies correlation with CO (as in work by *Dunse et al.* [2005]), are extrapolations from SE Australian regional emissions (which impact on Cape



**Figure 6.** Annual estimates of emissions of HFC-125 ( $\text{kt yr}^{-1}$ ) from the EU-15 region based on AGAGE in situ measurements using the correlation method with CO, UNFCCC data (2008 submission), modified UNFCCC data (McCulloch), and NAME model.





**Figure 7.** Annual estimates of emissions of HFC-125 ( $\text{kt yr}^{-1}$ ) from the United States based on UNFCCC data (2007 and 2008 submissions), McCulloch, and the NAME model.

Grim), on a population basis. The NAME model scales emissions based on the population of two states of Australia, Tasmania and Victoria, amounting to 5.4 million people (2006 census) which is 25% of the population of Australia. The estimates of emissions based on correlation of HFC-125 and CO data at Cape Grim are lower than the emissions reported to the UNFCCC (by 68% in 2006), which in turn are significantly lower than the McCulloch (by 83% in 2005) and NAME model estimates (by 77% in 2006). It is interesting most of the methods show a year on year increase, but that both measurements based estimates show a slower rate of increase than bottom-up estimates. *Energy Strategies* [2008] independently estimated Australian emissions for HFC-125, in addition to HFC-134a and HCFC-22. The report did resolve the large differences between the UNFCCC and AGAGE estimates for HFC-125. *Energy Strategies* [2008] reported emission for 2006 which are in reasonable agreement with ( $\sim 10\%$  lower than) with the Australian UNFCCC values. There has been a third independent bottom-up estimate of HFC-125 imports and emissions in Australia [*Department of the Environment, Water, Heritage and the Arts (DEWHA)*, 2008]. For 2006, this report estimates the consumption (imports minus exports) of HFC-125 in Australia to be 870 tonnes and the emissions to be 250 tonnes, very close to the estimates submitted by the Australian government to the UNFCCC (260 tonnes).

[33] The interspecies correlation technique calculates HFC-125 emissions for the SE Australian region that are significantly lower than all five estimates of emissions from other top-down (NAME) or bottom-up methods (Table 7). The interspecies correlation (to CO) method is susceptible to significant bias if there are unaccounted for CO emissions in the SE Australian region, for example from biomass burning. We are investigating methods to ensure that the interspecies correlation technique is not biased by biomass burning.

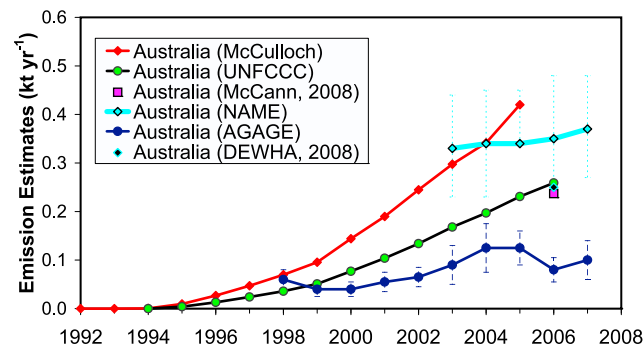
#### 4. Conclusions

[34] Continuous measurements of HFC-125 have been made at five AGAGE stations and two SOGE stations between 1998 and 2008. These measurements indicate that the atmospheric accumulation since 1998 has been midway

between linear growth and exponential growth. The growth rate was  $0.8 \text{ ppt yr}^{-1}$  ( $16\% \text{ yr}^{-1}$ ) in 2007. The mole fraction in the global lower troposphere at the beginning of 2008 was estimated to be 5.6 ppt. The continuous data record was extended back in time to 1978 by analysis of NH and SH archived air samples. In general the calculated seasonal cycles typically do not differ from zero by more than the one sigma level of confidence, but they are consistent with the seasonal cycles measured by AGAGE in many other gases at Mace Head and Cape Grim. The NH-SH transport seasonality was calculated to have a larger contribution than the in situ variations of OH to the seasonal cycle in HFC-125 at Cape Grim. In contrast, the seasonal cycle at Jungfraujoch was found to be strongly influenced by the close proximity of this observatory to the top of the atmospheric boundary layer resulting in enhanced transport of polluted air masses from the surrounding European polluted boundary layer.

[35] Global emissions were calculated using the AGAGE 2-D 12 box model. These results indicated that HFC-125 has been increasing by about  $15\% \text{ yr}^{-1}$  since 2000 and that emissions were approximately  $21 \text{ kt yr}^{-1}$  in 2007. There is relatively good agreement with estimates based on industrial production as reported to the UNFCCC (but including some estimates for East Asia added by A. McCulloch). Estimates based on industrial production are slightly smaller than those calculated from the measurements.

[36] Regional emission estimates were compared for methods using AGAGE measurements (top-down approach) to those based on national inventories (bottom-up approach). Emission comparisons varied from year to year, however comparing estimates for 2005, the EU15 countries the estimates ranged from  $2.7 \text{ kt yr}^{-1}$  (UNFCCC) to  $4.7 \text{ kt yr}^{-1}$  (McCulloch, also bottom-up estimate); the top-down estimate was  $3.6 \text{ kt yr}^{-1}$ , but the top-down estimates were typically closer to the McCulloch than to the UNFCCC estimates. For the United States, McCulloch and UNFCCC (2007) produced a similar estimate of approximately  $7.3 \text{ kt yr}^{-1}$ , whereas UNFCCC (2008) estimated just  $3.7 \text{ kt yr}^{-1}$ . A top-down estimate extrapolated from measurements at Trinidad Head, California was  $1.8 \text{ kt yr}^{-1}$  (used 2006 since we do not have an estimate for 2005). For Australia in 2005 the McCulloch estimate was largest



**Figure 8.** Annual estimates of emissions of HFC-125 ( $\text{kt yr}^{-1}$ ) from Australia based on AGAGE in situ measurements using the CSIRO interspecies correlation method with CO [Dunse *et al.*, 2005], from UNFCCC data (2008 submission), McCulloch, the NAME model, *DEWHA* [2008], and *Energy Strategies* [2008].

**Table A1.** National Percentages of Each Year's Emissions of HFC-125 From Within the EU<sup>a</sup>

Country <sup>b</sup>	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
Austria					0.06	1.46	2.73	2.96	2.48	1.73	1.66	1.77	1.80	1.72	1.73	1.73
Belgium		43.82	59.60	5.53	1.73	0.88	1.97	2.60	3.37	3.52	3.57	3.50	3.61	3.53	3.43	3.38
Bulgaria																
Czech Republic						0.74	2.90	0.39	1.97	0.72	1.38	1.20	1.75	1.72	1.54	
Denmark					0.56	2.56	4.50	4.26	3.79	3.63	3.61	2.89	2.51	2.28	2.17	2.19
Estonia																
Finland					0.15	1.62	2.19	2.21	3.15	3.93	2.75	3.30	1.71	2.43	2.51	2.66
France				0.22	4.11	6.15	6.72	7.63	7.63	8.95	11.49	13.04	14.73	16.00	15.50	15.68
Germany				13.64	21.50	27.76	28.44	27.64	26.51	23.27	20.96	18.90	17.62	16.22	16.77	17.08
Greece											0.07	0.17	0.35	0.81	1.36	1.22
Hungary								0.32	1.26	2.69	1.54	1.54	2.01	1.90	1.84	1.48
Ireland		56.18	40.40	2.62	0.66	0.30	0.36	0.61	0.81	0.65	0.54	0.41	0.44	0.53	0.64	0.64
Italy						0.65	1.83	2.35	5.97	8.76	11.13	12.93	14.60	15.51	17.23	18.95
Latvia																
Lithuania																0.04
Luxembourg			3.05	0.78	0.34	0.18	0.11	0.08	0.06	0.26	0.22	0.20	0.18	0.16	0.32	
Netherlands					2.50	4.33	4.26	3.59	2.49	2.65	2.76	2.80	2.71	2.79	2.83	
Poland											2.45	3.00	3.10	3.49	3.05	2.72
Portugal							0.19	0.24	0.27	0.35	0.41	0.45	0.44	0.44	0.42	0.48
Romania														0.01		
Slovakia						0.01	0.03	0.05	0.07	0.08	0.15	0.21	0.29	0.33	0.36	0.40
Slovenia																
Spain							1.74	2.81	3.33	3.39	3.49	3.45	3.43	3.26	3.30	3.35
Sweden				9.76	6.38	4.69	3.15	2.35	1.90	1.45	1.28	1.08	1.04	0.89	0.79	0.76
UK				65.19	64.08	51.08	40.91	36.70	35.40	33.06	31.26	28.99	28.13	26.02	24.22	22.55

<sup>a</sup>Values are given as percent.

<sup>b</sup>Cyprus and Malta are not "Annex 1" Parties to the Kyoto Protocol and do not report emissions in the same way as other European countries.

(0.42 kt yr<sup>-1</sup>), whereas the UNFCCC based estimates (for example 0.23 kt yr<sup>-1</sup>) were typically intermediate between two sets of measurement based estimates. The variations between the different approaches in these comparisons, shown in Figures 6–8 and Tables 5–7, highlight likely limitations of each of the methods used but they also emphasize the need for such comparisons in an attempt to determine and verify emissions more accurately.

## Appendix A: Calculation of National Emissions

[37] Given that emissions of fluorocarbons such as HFC-125 arise during use of the fluid or on disposal of the systems containing it, the quantities emitted are rarely, if ever, measured directly and have to be calculated, with significant uncertainty. Conversely, the amounts that are produced and sold (consumption) can be ascertained from manufacturers' and importers' statistics with much more certainty.

[38] In the country studies that underlie much of the data placed in the UNFCCC database, emissions are calculated from an inventory in equipment that may, or may not, be reconciled with recorded national consumption [McCulloch, 2009]. In this work emissions are calculated directly from consumption, either for individual countries such as United States where such data are provided, or for economic units, such as the EU. In the latter case, the UNFCCC data provided a distribution function to allocate emissions between member states.

[39] HFC-125 is used in refrigeration from which there are three modes of release: losses during the first fill of equipment, releases during operation from leaky systems or when the systems are serviced and releases during disposal of the equipment at the end of its useful life. The relative rates of emission from these modes were characterized for

CFCs [Gamlen *et al.*, 1986]. Despite considerable advances in technology, the same relative rates appear to describe accurately emissions of HFC-134a [McCulloch *et al.*, 2003]. It appears that the advances in technology have resulted in significant reductions in the absolute rate of loss of fluid into the environment but service intervals and overall equipment lifetime are dictated by economic considerations, consequently the reduced absolute loss rates have translated into less fluid in the equipment. This has also resulted in lower fluid requirements to meet an increasing demand for refrigeration.

### A1. European Union

[40] Table A1 shows the fraction of annual total European emissions of HFC-125 accountable to each country and was calculated from the national statistics reported in Table A2(II)s1 in the Common Reporting Format to UNFCCC (available at unfccc.int). With the exception of Luxembourg, the Netherlands and UK, the data reported were the actual tonnes of emissions of HFC-125 from country studies estimated using the number of pieces of refrigeration equipment and emission functions from within the standard range specified by IPCC [1997]. For the named countries, some or all of the emissions were aggregates of all HFCs, from which the HFC-125 content was calculated using its annual fraction of European emissions.

[41] The combined EU data are far from homogeneous, with annual emission rates (the fraction of the remaining "bank" of refrigerant emitted each year) varying by up to a factor of five between countries with very similar economies and demands for refrigeration. The differences lie in the way that each country carries out its survey of equipment and in the emission factors chosen for that pool of equipment but relative amounts have less systematic error

Table A2. Annual Emissions of HFC-125 From EU<sup>a</sup>

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
Total EU as reported		0.41	0.60	9.65	41.12	100.93	210.38	370.07	575.01	873.20	1192.55	1560.72	1935.03	2412.72	2761.98	3096.34
Emission expected from Sales				19.17	57.96	152.92	320.05	567.98	900.91	1323.45	1837.68	2450.12	3155.57	3902.88	4805.13	5607.23
Factor		1.99	1.41	1.52	1.52	1.52	1.52	1.53	1.57	1.52	1.54	1.57	1.63	1.62	1.74	1.81
Country																
Austria				1.06	0.04	2.23	8.72	16.82	22.34	22.83	30.53	43.36	56.83	67.15	83.13	96.92
Belgium					1.00	1.35	6.31	14.76	30.33	46.59	65.63	85.75	113.88	137.63	164.79	189.52
Bulgaria																
Czech Republic					0.32	3.91	2.37	16.46	3.48	26.12	13.30	33.78	37.98	68.16	82.43	86.27
Denmark							14.39	24.22	34.19	48.09	66.36	70.72	79.10	88.80	104.18	122.66
Estonia																
Finland					0.08	2.48	7.00	12.57	28.37	52.06	50.57	80.91	53.82	94.95	120.60	148.87
France			0.04	2.61	2.38	9.41	21.51	43.35	68.73	118.45	211.06	319.61	464.70	624.45	744.85	879.03
Germany			2.61	2.61	12.46	42.44	91.01	156.97	238.81	308.00	385.11	462.99	555.87	632.86	805.91	957.86
Greece											1.26	4.23	11.08	31.58	65.54	68.23
Hungary								1.81	11.34	35.62	28.34	37.81	63.38	74.29	88.25	83.19
Ireland			0.50	0.50	0.39	0.47	1.14	3.44	7.32	8.61	9.89	10.07	13.82	20.68	30.82	35.72
Italy						1.00	5.87	13.34	53.82	115.96	204.46	316.69	460.84	605.47	828.09	1062.73
Latvia															0.10	0.02
Lithuania																2.14
Luxembourg					0.58	0.52	0.57	0.64	0.73	0.80	4.85	5.33	6.28	6.95	7.79	18.14
Netherlands						3.83	13.84	24.18	32.37	33.01	48.69	67.66	88.38	105.91	134.02	158.50
Poland											45.02	73.55	97.81	136.35	146.64	152.64
Portugal							0.59	1.37	2.41	4.59	7.61	10.93	14.02	16.99	20.08	26.94
Romania											0.06	0.03	0.06	0.24	0.23	0.19
Slovakia						0.01	0.11	0.28	0.64	1.10	2.85	5.14	9.10	12.79	17.13	22.59
Slovenia																
Spain			1.87	1.87	3.70	7.17	10.08	13.35	17.10	19.18	23.50	26.56	32.82	34.62	37.88	42.64
Sweden							130.94	208.45	318.92	437.57	574.54	710.36	887.68	1015.63	1163.94	1264.49
UK			12.50	12.50	37.14	78.11	130.94	208.45	318.92	437.57	574.54	710.36	887.68	1015.63	1163.94	1264.49

<sup>a</sup>Values are given as metric tonnes.

**Table A3.** Data From United States

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
Quantity sold tonnes <sup>a</sup>	0.00	0.00	1218.51	1580.53	1988.06	3230.75	4223.66	4990.46	5785.90	5557.56	6506.90	7184.46	8218.38	9397.99	10674.40	14244.51
Reported Emissions tonnes <sup>b</sup>	0.00	0.00	200.71	460.44	749.16	1267.31	1841.40	2485.39	3091.08	3514.10	3981.97	4421.79	4899.54	5481.18	6172.13	7059.08
Emissions calculated from sales	0.00	0.00	85.30	208.12	424.01	773.44	1244.60	1816.72	2458.98	3109.13	3799.22	4438.90	5074.94	5736.24	6484.73	7499.24
Emissions used here tonnes	0.00	0.00	200.71	460.44	749.16	1267.31	1841.40	2485.39	3091.08	3514.10	3981.97	4421.79	5074.94	5736.24	6484.73	7499.24

<sup>a</sup>These data were reported in the 2007 submission.

<sup>b</sup>Using the same emission functions as those used to calculate total European emissions from total European sales.

than the absolute quantities reported by each country [McCulloch, 2009].

[42] Total European sales of HFC-125 are collected under European legislation and supplement the prior database maintained by industry and provide a more certain basis from which to calculate emissions than estimates of the number and variety of items of equipment. These sales data were combined with the overall emission functions used effectively for other fluorocarbons [McCulloch *et al.*, 2003] to derive total European annual emissions. The reported annual totals and those calculated in this way are shown in Table A2.

[43] European emissions calculated from sales exceed those estimated from equipment by a large margin in all years and, since it has been demonstrated that the equipment method consistently underestimates emissions (IPCC/TEAP [Campbell and Shende, 2005]), the data calculated from sales were used here. The remainder of Table A2 shows national emissions calculated using national percentages of the European total.

## A2. United States

[44] Data reported by the United States include annual sales of HFC-125 and, using these data, calculated emissions of HFC-125 in many years are lower than those reported, which is the exact opposite of the situation with European data. The greater of each annual pair of values was used here for the global database, see Table A3. The data submitted by the United States in 2008 have a completely different (generally smaller) set of numbers for the annual quantities produced. There is no explanation for this in the accompanying National Inventory Report and so there is no means of deciding whether or not one set is more “accurate” than the other and the original data have been used here.

## A3. Other Countries

[45] Of the 12 additional countries that report greenhouse gas emissions, only Australia, Canada, Japan, New Zealand, Norway and Switzerland report HFC-125; in most cases reporting emissions only, not consumption. For the global database reported emissions were used in the case of countries reporting consumption. The emissions from those countries that did not report consumption were increased using the factors derived for annual European emissions. Although this is somewhat arbitrary, it was judged to provide a more consistent set of data than the reported emissions alone. The reported data and values included in the database are shown in Table A4. Developing countries, in the case of HFC-125 particularly China, are not obliged to report emissions to UNFCCC. The Chinese production and emissions were assigned annual values equal to 3% of the global annual totals, consistent with the estimate of non-reported production of HFCs provided by AFEAS for this period (Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), <http://www.afeas.org>, 2008). In recent years there has been a dramatic growth in HFC production in China and the allowance of 3% cannot be applied to the data.

## A4. Uncertainty

[46] Given the diverse ways that countries calculate the emissions used as the source data here and the high

Table A4. Data From Other Reporting Countries<sup>a</sup>

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
	<i>Reported Emissions</i>															
Australia						4.36	13.00	23.72	36.44	51.32	76.59	104.34	134.42	168.48	197.43	230.54
Canada				0.13	18.12	18.12	31.50	76.70	113.09	149.44	179.15	212.36	238.81	272.71	303.29	298.63
Japan									1.60	6.44	13.56	33.46	40.26	52.96	92.04	112.21
New Zealand				1.20	0.50	0.50	6.70	10.50	9.50	10.40	4.10	27.60	47.60	53.90	49.50	62.40
Norway				0.47	2.38	2.38	5.47	9.64	14.60	19.73	25.82	33.01	38.79	41.93	44.76	47.21
Switzerland			0.02	0.42	1.24	2.99	5.64	9.03	11.78	16.62	23.37	30.05	31.53	38.66	44.17	45.13
	<i>Values in Database</i>															
Australia				0.34	9.67	40.17	26.97	47.05	69.74	95.67	143.95	189.93	244.73	297.55	341.48	417.50
Canada							65.38	152.16	216.44	278.57	336.72	386.58	434.79	481.64	524.56	540.79
Japan									3.07	12.00	25.48	60.90	73.31	93.54	159.18	203.21
New Zealand				3.09	1.11	1.11	13.90	20.83	18.18	19.39	7.71	50.24	86.66	95.19	85.61	113.00
Norway				0.47	2.38	2.38	5.47	9.64	14.60	19.73	25.82	33.01	38.79	41.93	44.76	47.21
Switzerland			0.02	0.42	1.24	2.99	5.64	9.03	11.78	16.62	23.37	30.05	31.53	38.66	44.17	45.13

<sup>a</sup>Values are given as metric tones.

probability of systematic bias, as discussed above, a formal error analysis for country data is not possible. Subjectively, the values for individual countries could differ from their actual emissions by a factor of two (based on the factors relating reported data to emissions calculated from sales in Europe). Overall, uncertainties are much lower. Over three-quarter of the emissions arise from sales that are reported with an uncertainty less than 10%. The global functions relating emissions to sales are of a similar level of accuracy and so the error in the annual global total emissions is likely to be about 25%.

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