Observations of 1,1-difluoroethane (HFC-152a) at AGAGE and SOGE monitoring stations in 1994–2004 and derived global and regional emission estimates


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Ground-based in situ measurements of 1,1-difluoroethane (HFC-152a, CH₂CHF₂) which is regulated under the Kyoto Protocol are reported under the auspices of the AGAGE (Advanced Global Atmospheric Gases Experiment) and SOGE (System of Observation of halogenated Greenhouse gases in Europe) programs. Observations of HFC-152a at five locations (four European and one Australian) over a 10 year period were recorded. The annual average growth rate of HFC-152a in the midlatitude Northern Hemisphere has risen from 0.11 ppt/yr to 0.6 ppt/yr from 1994 to 2004. The Southern Hemisphere annual average growth rate has risen from 0.09 ppt/yr to 0.4 ppt/yr from 1998 to 2004. The 2004 average mixing ratio for HFC-152a was 5.0 ppt and 1.8 ppt in the Northern and Southern hemispheres, respectively. The annual cycle observed for this species in both hemispheres is approximately consistent with measured annual cycles at the same locations in other gases which are destroyed by OH. Yearly global emissions of HFC-152a from 1994 to 2004 are derived using the global mean HFC-152a observations and a 12-box 2-D model. The global emission of HFC-152a has risen from 7 Kt/yr to 28 Kt/yr from 1995 to 2004. On the basis of observations of above-baseline elevations in the HFC-152a record and a consumption model, regional emission estimates for Europe and Australia are calculated, indicating accelerating emissions from Europe since 2000. The overall European emission in 2004 ranges from 1.5 to 4.0 Kt/year, 5–15% of global emissions for 1,1-difluoroethane, while the Australian contribution is negligible at 5–10 tonnes/year, <0.05% of global emissions.


1. Introduction

The implementation of the Montreal Protocol has led to changes in production, use and emissions of chlorine (Cl) and bromine (Br) containing chemicals in key applications such as refrigeration, foam blowing, aerosol propellants and industrial solvents. Chemicals such as the chlorofluorocarbons (CFCs) and some C₁–C₂ chlorofluorocarbons have contributed substantially to the depletion of stratospheric ozone observed from midlatitudes to the poles in both hemispheres. The intermediate chemicals used as replacements (the hydrochlorofluorocarbons (HCFCs), principally HCFC-22 (CHClF₂), HCFC-141b (CH₂ClCF₂) and HCFC-142b (CH₃CClF₂)) also contain Cl so their release into the atmosphere contributes to the tropospheric and stratospheric Cl loading and hence to ozone depletion. Currently, hydro-
fluorocarbons (HFCs, particularly HFC-134a (CH₂FCF₃)) are used as chlorine-free substitutes predominantly in applications which, previous to the Montreal Protocol, employed CFCs. Global and regional emission patterns of Cl and fluorine (F) containing chemicals have changed significantly in the last 20 years as the transition has been made to those species which prove less harmful to the stratospheric ozone layer and enhanced performance in commercial applications. However, emission of fluorine containing gases such as HCFCs and HFCs is not without environmental consequences. These chemicals possess strong infrared absorptions in the 8–12 μm spectral region, enhancing radiative forcing. The changing emission patterns of F and Cl-containing gases have been monitored through long-term observations of the concentrations of these chemicals in the global atmosphere. Emission estimates of gases regulated under both Montreal and Kyoto Protocols from global observations is a vital component of assessing the effectiveness of such international treaties.

Emission estimates of radiatively important species are based either on production and consumption/usage data (bottom-up) or on inverse methods that use observed concentrations to derive regional and global emission source locations and strengths (top-down). Top-down global inversion methods rely on accurate estimates of parameters such as rates and mechanisms of chemical and physical removal processes in the atmosphere, the atmospheric lifetime of a species, whereas regional inversion methods assume negligible loss within the regional domain. The inverse methods rely upon accurate and precise global/regional observations of chemicals at various locations. The most useful locations for deriving both global and regional emissions are those which combine observing the average background concentrations while also capturing emission events from known sources (the latter principally in the Northern Hemisphere, where anthropogenic production, use and emissions are predominant). Accurate emission estimates of the key CFCs, HCFCs and HFCs are important in order to assess the impact they have upon radiative forcing and ozone depletion now and in the future. Ideally, the emission estimates derived using top-down and bottom-up estimation methods should agree to within their respective uncertainties [Ehhalt et al., 2001]. However, estimating emissions from a limited number of observation sites becomes difficult for compounds which have short atmospheric lifetimes (<2 years) and therefore have removal rates comparable to the timescales of global transport processes.

HFC-152a (1,1-difluoroethane, CH₃CF₂) is used predominately in foam-blowing and aerosol spray applications as a replacement compound for CFCs [Ashford et al., 2004a]. Various reaction mechanisms have been proposed for the removal of HFC-152a from the atmosphere. Kinetic studies on reaction rates for CH₃CF₂ with O (³P) [Zhang et al., 2004; Liu et al., 2004], with O (¹D) [Kono and Matsumi, 2001] and OH radicals [Kozlov et al., 2003; Wilson et al., 2003], have been reported. The conclusion is that the environmental fate of emitted HFC-152a is dominated by reaction with the OH radical in the troposphere. A range of atmospheric lifetimes has been proposed for HFC-152a, on the basis of its measured OH reaction rate, the OH concentration, and the estimated distribution of its emissions. Prather and Spivakovsky [1990] estimated its tropospheric lifetime to be 1.65 years for reaction with OH, with a total lifetime of 1.53 years, while Ravishankara and Lovejoy [1994] estimated a total lifetime of 2.0 years. The IPCC 2001 value is 1.4 years [Ehhalt et al., 2001], the same as is obtained by Kozlov et al. [2003], using the CH₃CCl₃ (methyl chloroform) based OH estimate of Prinn et al. [1995]. Hydrogen abstraction from CH₃CHF₂ (HFC-152a) by OH, yields CH₃CF₂O as an intermediary product, which ultimately will degrade to COF₂ either directly or via the intermediate alkyl peroxide CH₃CF₂OOH [Hashikawa et al., 2004]. COF₂ is incorporated to the aqueous phase (clouds, rain or seawater), followed by hydrolysis, to yield CO₂ [Wallington et al., 1994].

riters et al., 2000; Fraser et al., 2003; Krummel et al., 2004, 2006]. The HFC-152a annual means and growth rates have grown from 0.8 ppt (0.1 ppt/yr growth rate) in 1998 to 1.8 ppt (0.4 ppt/yr growth rate) in 2004. Melbourne emissions of HFC-152a have been estimated from Cape Grim ADS-GCMS data to be 1–2 tonnes/yr for 1998–2003 [Dunse et al., 2005a].

The World Meteorological Organisation (WMO) 2002 ozone assessment [Montzka et al., 2003] reports the Southern Hemispherical HFC-152a values reported by Sturrock et al. [2001] increasing at 0.2 ppt/yr (12%/yr) from 1998 to 2000. The Intergovernmental Panel on Climate Change (IPCC) 2001 [Ehhalt et al., 2001] estimate HFC-152a emission in the late 1990s of 4 Gg (Kt) per annum and predict global abundances of 55 ppt and 80 ppt by 2050 and 2100 respectively. More recently, the IPCC, jointly with the Technology and Economic Assessment Panel (TEAP) of the Montreal Protocol [Velders et al., 2005] lists 2003 HFC-152a abundances of 2.6 ppt (global average) and 4.1 ppt (European average) with 2001–2003 growth rates of 0.34 ppt/yr and 0.60 ppt/yr for global and European observations respectively. HFC-152a emission estimates have risen from 0.5 Kt/yr to 2.0 Kt/yr for Europe during 1995–2003, while global estimated HFC-152a emissions have risen from approximately 1 Kt/yr in 1994 to 20–22 Kt/yr by 2002–2003 [Velders et al.,
The reported abundances and emissions of HFC-152a in the IPCC/TEAP report [Felders et al., 2005] have been compiled from data we update and present more comprehensively in this work. In the same report, global HFC/HCFC emissions are derived from production/consumption/end-use modeled data. The consumption-based estimate of 4 Kt/yr HFC-152a in 2002 will become virtually unchanged by 2015 in a business-as-usual emission scenario [Campbell et al., 2005]. The authors note that emission estimates for certain HCFC/HCFCs will not agree between those derived from observations and those derived from production/consumption/end-use models because of unavailability of production data because of antitrust laws where there are less than three manufacturers for the same chemical, such as HFC-152a [Campbell et al., 2005].

Previous reports by some of the authors of this manuscript include HFC-152a observations and derived emissions as a minor segment of larger works using a less comprehensive data set. We fully update the current state of knowledge regarding HFC-152a abundance, long-term atmospheric growth rate and seasonal behavior in the atmosphere in this manuscript. The most recent observational data of HFC-152a in Europe and Australia have been inputted to our updated emission models to reevaluate, construct and comprehensively update global and regional emission estimates for HFC-152a from 1995 to 2004. Regional source allocations using updated back trajectory techniques are detailed to provide the geographical sources of HFC-152a emissions in Europe. Observational data for HFC-152a from the AGAGE sites are now provided online to the scientific community via the Carbon Dioxide Information Analysis Centre (CDIAC) website (http://cdiac.esd.ornl.gov/ndps/alegage.html).

2. Experimental Methods

High-frequency observations (fully calibrated air samples every 4 hours) of HFC-152a have been undertaken at two field locations as part of the AGAGE program since 1994 (Mace Head, Ireland) and 1998 (Cape Grim, Tasmania). Similar observations have been made by the System of Observation of halogenated Greenhouse gases in Europe (SOGE) program since 2000 at Jungfraujoch, Switzerland and since 2001 at Zeppelin Station, Spitzbergen and Monte Cimone, Italy [Grealy et al., 2002; Reimann et al., 2004]. The method involves using a custom built preconcentration system (Adsorption Desorption System (ADS)) to selectively retain halogenated compounds from 2 liter air samples. After rapid thermal desorption the target halocarbons are separated and quantified using a commercial gas chromatograph–mass spectrometer (GC-MS) system (Agilent 6890 GC, 5973 MS) [Simmonds et al., 1995; Maione et al., 2004]. The enrichment technique allows quantitative retention of HFC-152a (among ~25 other halocarbons) from sampled air or calibration standard to yield an approximate limit of detection (S/N >3) of 0.25 ppt (10⁻¹² mole fraction). The measurement precision varies between monitoring stations, but on average a relative standard deviation of 5% or better is achieved. Fuller descriptions of the measurement and calibration techniques are given by Simmonds et al. [1995], Prinn et al. [2000] and O’Doherty et al. [2004]. All 5 monitoring stations use a common calibration scale (UB-98), propagated from commercially available gravimetric standards (Linde Gases, U.K.) through secondary standards (“Gold” standards) and finally through to site-specific working standards [O’Doherty et al., 2004; Reimann et al., 2005]. Hence the emission estimates derived from monitoring sites in AGAGE and SOGE are unlikely to be biased by differences in measurement calibration.

3. Results and Discussion

3.1. In Situ Observations

3.1.1. Baseline HFC-152a

The complete set of atmospheric HFC-152a observations is shown in Figure 1 for all 5 monitoring sites. The data set extends from 1994 to 2004 for Mace Head, Ireland, 1998 to 2004 for Cape Grim, Tasmania, 2000 to 2004 for Jungfraujoch, Switzerland and 2001 to 2004 for both the Zeppelin Station, Spitzbergen and Monte Cimone, Italy. The observation data are segregated into baseline and above-baseline data in order to aid interpretation, trend analysis and to generate emission estimates.

Several methods are used to define baseline observations. In the first method, employed in AGAGE, the baseline is defined statistically using a filtering algorithm; points from the data set which are more than 3 standard deviation above the average baseline are then removed [Prinn et al., 2000; O’Doherty et al., 2001; Cunnold et al., 2002]. The AGAGE baseline filter method has been applied to data from all stations. The second method (used at Mace Head-only) utilizes the NAME dispersion model and analysis meteorology to exclude data obtained when the air being sampled has originated over the landmass of the European continent or over the British Isles [Ryall et al., 2001; Manning et al., 2003]. In the NAME method, the filtering is driven by meteorology and baseline conditions are generally seen when the air masses arriving at the station are from the north to northwest (Greenland/Iceland/Arctic) or from the west to southwest (Atlantic/USA/Canada). Air masses with a tropical air component are excluded from the baseline analysis because of a strong latitudinal gradient. The NAME model excludes data from the baseline definition which are local to the observation station, defined by low wind speed and a boundary layer thinner than 300 m. The NAME model meteorology cannot be used currently to adequately represent mountainous stations and tends to under represent the complex meteorology of the Alps. As yet, the NAME model has not been applied to Cape Grim data. The third method applied to the Jungfraujoch, Monte Cimone and Mace Head stations uses a model combining 48-hour back trajectories (from the Swiss Meteorological Institute (MeteoSwiss)) with the average (2002–2004) instrumental precision for HFC-152a to define above-baseline HFC-152a as data which is greater than the instrumental precision. In this method, described by Reimann et al. [2005] and summarized here, the average instrumental precision is deduced from the analysis of the calibration standard before and after each air analysis, corrected for the absolute detector response drift. After the initial iteration to remove data points beyond ±2 S.D. from the baseline, second and subsequent iterations remove the next level of data points which fall above and below ±2 S.D. units from the residual. The iteration continues until no remaining
points can be removed and the remaining data points are smoothed and plotted to define the observational baseline. 

[11] The AGAGE derived baselines from the in situ observations are shown as black points in Figure 1. Figure 2 shows the monthly mean baseline data which are used to define a long-term growth rate for HFC-152a. The yearly trend in the baseline (AGAGE filter) and the annual mean mixing ratio in 2004 is presented in Table 1 and illustrated in Figure 3. The European sites exhibit similar growth rates for HFC-152a of between 15 and 20%/yr. All the European stations exhibited a pronounced growth rate change in 2002, increasing from 13%/yr in 2000–2001 to 16–20%/yr in 2002–2003, with a slower growth rate of 12% in 2004. This effect could be due to decreased emission of HFC-152a in the Northern Hemisphere (NH) during 2004. It is also possible that the growth rate yearly variation is influenced by the extent of Northern Hemisphere tropospheric exchange to either the Southern Hemisphere (SH) troposphere or the stratosphere. Baseline concentrations of HFC-152a also increased over this period at Cape Grim, by 19% in 2002, 8.7% in 2003 and 23% in 2004.

[12] HFC-152a has a large interhemispheric gradient due to its short atmospheric lifetime through rapid removal by OH. Distinct below-baseline events (10–15% below the average baseline) are seen at Mace Head when the sampled air mass originates from tropical regions. An example is shown in Figure 4 for 26 January 2003 showing below-baseline deviation for HFC-152a (–15%) alongside smaller deviations for HFC-134a, HCFC-142b and HCFC-141b (–5%, –4% and –4% respectively). Similar below-baseline events for HFC-152a are observed at the Jungfraujoch and Monte Cimone stations when air originates from higher altitudes and lower latitudes. Such meteorological events would be interpreted and included as baseline using the AGAGE filtering method. The NAME filter provides a

Figure 1. Observations of HFC-152a at AGAGE and SOGE monitoring stations. Data shown with a filtering split between baseline (solid) and above-baseline (shaded) derived using the AGAGE filtering method. (a) Mace Head, (b) Jungfraujoch, (c) Zeppelin, (d) Monte Cimone, and (e) Cape Grim.
differing definition of baseline to the AGAGE filter as the meteorology function excludes below-baseline events from the defined baseline. Because southerly transport to Mace Head is infrequent, there is virtually no difference in the baseline average monthly means derived from either the AGAGE or NAME filtering for HFC-152a.

3.1.2. Annual Cycles in HFC-152a

The cycle for HFC-152a is driven by reaction with the OH radical, the predominant removal mechanism for HFC-152a in the troposphere. The annual cycles in HFC-152a are illustrated in Figure 5. For each observation station, two mean averaged cycles are coplotted. The solid lines illustrating the average annual cycle over the total measurement period and the dashed lines show the mean cycle for 2002–2004 only, a common observation period for the five stations. The European sites have similar maxima in spring (April/May) and minima in autumn (September), as would be expected given the higher OH abundance in the summer. Conversely, the annual cycle at Cape Grim show the maxima in the Southern Hemisphere in September, with the minima observed in March, again consistent with the different seasons in the Southern Hemisphere.

The rate of increase in the HFC-152a baseline is exponential, as detailed above. Consequently the amplitude of the annual cycle should increase exponentially from early to later years given that it is the product of the concentration of OH and concentration of HFC-152a in the atmosphere. A theoretical analysis of the baseline annual cycle was performed using the AGAGE 12-box model described by Cunnold et al. [1997]. The resulting simulation of the Mace Head and Cape Grim annual cycle suggests that the amplitude of the cycle should have increased by about a factor of approximately 3 from 1996 to 2004. The increased amplitude, however, is not exponential because of variability in the annual cycle estimates from each year of HFC-152a measurements in the Northern Hemisphere. Atmospheric transport will also have an effect on the year-to-year maxima and minima in the observed annual cycles. Figure 5 shows that the 3-year (2002–2004, dashed line) average amplitude for Mace Head is approximately 1.6 times greater than the 10-year (1994–2004, solid line) average from the observations, this concurs with the 12-box model prediction of 1.6 times. In addition, an appreciable difference is observed between the 3-year (2002–2004, dashed line) and 6-year (1998–2004, solid line) average at Cape Grim of 1.5, almost identical to the 1.4 times increase predicted using the 12-box model. The increased amplitude of the annual cycle observed at Cape Grim is more noticeable because of the lesser effect of emission variability in the Southern Hemisphere, whose baseline annual cycle will be determined mainly by a combination of interhemispheric transport from Northern Hemispheric emissions and reaction of HFC-152a with OH.

The cycles for Mace Head and Zeppelin are smoothest in appearance after baseline filtering, because these stations more frequently sample baseline conditions. Conversely, the observed annual cycles at Jungfraujoch and particularly at Monte Cimone are not smooth. The annual cycle technique requires a significant proportion of data to be at baseline conditions throughout the year, a condition rarely met at the Swiss and Italian stations given their closer proximity to the major emission sources in Europe. The amplitude of the annual cycles are different between the European stations. In general, the amplitude is 0.2 ppt (6–7% of the mean baseline) for Mace Head and Zeppelin data sets (cleaner air, with less deviation) and greater for the Jungfraujoch and Monte Cimone sites (closer proximity to European sources), which show greater variation in the HFC-152a annual cycle amplitude (0.4–1.0 ppt, 7–20% of the mean).

The amplitude of the annual cycle for gases which are removed by reaction processes in the troposphere is driven by their atmospheric removal rates. For example, the short atmospheric lifetime (5 days) of CHClCCl2, driven by reaction with the OH radical, manifests in a much larger removal rate (1.4 times increase predicted using the 12-box model) [Simmonds et al., 2006]. In contrast, the seasonal cycles observed for CH3FCF2 (HFC-134a), whose dominant removal mechanism is also reaction with OH (but whose atmospheric lifetime is 12.7 years) is marked by a seemingly semiannual cycle, driven mostly by atmospheric transport rather than reaction with OH [O’Doherty et al.,

Table 1. HFC-152a Growth Rates Derived From Baseline In Situ Observations Using the AGAGE Statistical Filtering Method

<table>
<thead>
<tr>
<th>Station</th>
<th>Country</th>
<th>Location</th>
<th>Period</th>
<th>2004 Baseline, ppt</th>
<th>Growth Rate, ppt/yr</th>
<th>Growth Rate, %/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mace Head</td>
<td>Ireland</td>
<td>53°N, 9°W</td>
<td>1994–2004</td>
<td>4.6</td>
<td>0.35 ± 0.05</td>
<td>13.9 ± 2.1</td>
</tr>
<tr>
<td>Jungfraujoch</td>
<td>Switzerland</td>
<td>46°N, 7°E</td>
<td>2000–2004</td>
<td>5.1</td>
<td>0.59 ± 0.08</td>
<td>15.8 ± 2.3</td>
</tr>
<tr>
<td>Zeppelin</td>
<td>Norway (S.)</td>
<td>78°N, 11°E</td>
<td>2001–2004</td>
<td>4.9</td>
<td>0.64 ± 0.06</td>
<td>17.2 ± 1.2</td>
</tr>
<tr>
<td>Monte Cimone</td>
<td>Italy</td>
<td>44°N, 10°E</td>
<td>2002–2004</td>
<td>5.5</td>
<td>0.75 ± 0.63</td>
<td>15.4 ± 12.5</td>
</tr>
<tr>
<td>Cape Grim</td>
<td>Australia (T.)</td>
<td>41°S, 145°E</td>
<td>1998–2004</td>
<td>1.8</td>
<td>0.18 ± 0.03</td>
<td>13.8 ± 2.5</td>
</tr>
</tbody>
</table>
2004]. The amplitude of the annual cycle for HFC-134a is less than 1% peak-to-mean compared to our observed HFC-152a amplitude of 6–7%. The fact that HFC-152a peak-to-mean percentage deviation is between those of CHClCCl$_2$ and HFC-134a is therefore unsurprising, being more driven by reaction with OH than by transport.

### 3.1.3. Elevations Above the Baseline

The monthly mean baseline can be subtracted from the total monthly mean to generate a residual excess of above-baseline ("pollution") data. Above baseline events, as defined using the AGAGE filter algorithm, are presented in Figure 6. The magnitude of above-baseline events observed for HFC-152a are significantly less for the Zeppelin and Cape Grim sites compared to the other observation sites, because of their remoteness from emission locations in Europe (Zeppelin) and the low frequency and magnitude of Australian emissions detected at Cape Grim. The Jungfraujoch and Monte Cimone sites in closer proximity to the European continent exhibit a larger number and a higher magnitude of the above-baseline events than Mace Head on the fringes of Europe. All western European sites show an increase in the magnitude and frequency of above-baseline events from 2002 onward, which is assumed to be due to increased emissions of HFC-152a. The above baseline events are used in section 3.3 to determine regional emission estimates of HFC-152a for Europe and Australia.

### 3.2. Global Emission Estimates of HFC-152a Derived From in Situ Observed Baselines and Estimated Global Emission Based on Consumption Data

#### 3.2.1. Historical Global Emission Estimates Based on in Situ Observations of HFC-152a

A recursive weighted least squares (Kalman) filter and a two-dimensional (2-D) global model were used to deduce the global emissions of HFC-152a from the AGAGE observations at Mace Head and Cape Grim. The model has horizontal divisions at 90°N, 30°N, 0°, 30°S and 90°S and vertical divisions at 1000, 500, 200 and 0 hPa [Cunnold et al., 1994, 1997]. The method uses "reference" transport parameters between all regions and "reference" OH concentrations in the eight lower regions from the derived polynomial OH trend calculated by Prinn et al. [2005] derived inversely from AGAGE CH$_3$CCl$_3$ data. The model error analysis includes probable errors in all these model quantities. The 2-D model is very flexible and computationally efficient compared to three-dimensional (3-D) models. This enables multiple sensitivity runs to examine the effects of model transport and chemistry errors on our emission determinations [Prinn et al., 2005]. Tests using CH$_3$CCl$_3$ with a high-resolution 3-D model with interannually varying and observationally constrained meteorology confirm that the χ (monthly mean dry-air mole fraction) and σ (standard deviation) values at a particular station define well the large volume averages corresponding to the above 2-D model [Prinn et al., 2005].

[19] Estimates of unknowns contained in a vector $x$ and their errors contained in a matrix $P$ are updated with each new month of data using

\[
x(+)=x(-)+K(y_0-y)
\]

\[
P(+)=(I-KH)P(-)
\]

where the (gain) matrix $K$ is given by

\[
K=P(-)H^T(HP(-)H^T+R)^{-1}
\]

[20] The postscripts (–) and (+) denote values of $P$ and $x$ before and after use of each month’s data. The matrix $H$ (and its transpose $H^T$) contains the partial derivatives of the elements of the model-calculated values for $\chi$ (contained in vector $y$) with respect to the elements of $x$. $H$ is computed as a function of time using the same 2-D model used to calculate $y$. The matrix $R$ is diagonal with its elements being...
Figure 4. Below baseline HFC-152a event observed at Mace Head. (a) Data record highlighting below-baseline event on 26 January 2003 and (b) 7-day back trajectory indicating southern transport into Mace Head on 26 January 2003.
Figure 5. Annually averaged seasonal cycle for HFC-152a from GC-MS observations at (a) Mace Head (1994–2004), (b) Jungfraujoch (2000–2004), (c) Zeppelin (2001–2004), (d) Monte Cimone (2002–2004), and (e) Cape Grim (1998–2004). Solid lines indicate average for the period stated, and dashed lines in each panel represent the 2002–2004 average only.
the monthly variances \( (\sigma_k^2) \) associated with the observed \( \chi \) values at station \( k \) (contained in vector \( y_0 \)) augmented by an additional variance to account for model error [Prinn et al., 1995; Cunnold and Prinn, 1991]. The diagonal elements of \( P \) are the squares of the estimated errors \( \varepsilon_i \) in the elements \( x_i \) of the state vector \( x \). The Kalman filter uses \( \sigma_k \) rather than the smaller instrumental precision error in defining \( R \) in order to take account of the inability of the point measurements at the station to determine exactly the regional average \( \text{CH}_3\text{CCl}_3 \) concentrations for comparison with the 2-D model, sometimes called mismatch error [Prinn, 2000].

[21] The latest assessed rate constants for the reaction of OH with HFC-152a [Jet Propulsion Laboratory, 2003] are used. This gives an atmospheric lifetime for reaction with tropospheric OH of 1.56 years. It is assumed that the stratospheric destruction frequencies are the same as those for HFC-134a [Huang and Prinn, 2002] given the absence of UV cross sections for HFC-152a. These yield an atmospheric lifetime for stratospheric destruction of 19.5 years. The initial latitudinal distribution of HFC-152a emissions in the model used (1) reference emissions for HFC-134a [O'Doherty et al., 2004] and (2) a distribution with all emissions in the 30N–90N box. The best fit to the data was obtained with 30N–90N emissions only, and those results are reported here. A priori total reference emissions were estimated using a total atmospheric lifetime of 1.55 years. The 12-month running means of both observations and model calculations were compared. A seasonal cycle for OH is assumed alongside the annual OH estimates from Prinn et al. [2005] whose abundance varies significantly during the 1994–2004 observational period of HFC-152a reported here.

[22] The second-order polynomial fitting and annualized methods are both used to estimate the emissions [see, e.g., Prinn et al., 2005]. For the polynomial method emissions are fitted to the dimensionless expression \( f_p = a + bNP_1(t) + c(N^2/3)P_2(t) \) which multiplies the reference emissions. Here \( P_n \) is a Lengendre polynomial of order \( n \), and \( t \) is dimensionless time normalized to \( N \) and measured from the midpoint of the 2N-yearlong 1995–2004 interval. For the annualized method, only a value for the coefficient “\( a \)” is estimated each year. The error analysis for the polynomial and annualized methods are done using the sensitivity approach [see, e.g., Prinn et al., 2005] including the errors from the following sources: vertical OH gradients (biggest impact), OH concentrations, calibration, OH horizontal gradients, errors from Kalman filter, troposphere-stratosphere exchange time and stratospheric lifetimes (smallest impact). A 5% random error in calibration is assumed. Rate constant errors are also included in the polynomial method error analysis.

[23] The estimated global emissions as a function of year from 1995 to 2004 are presented in Table 2, derived only from the Mace Head and Cape Grim observation records, as these monitoring sites have sufficiently long observation records for such a long-term trend analysis. The polynomial method yields an accelerating rate of emissions over this time period. The annualized method shows the same general trend but with significant year-to-year variations, most of which include the polynomial estimates at the 1 sigma level when Kalman filter and model errors are included. The residuals between a final forward run of the model using the annualized optimal emissions and the AGAGE monthly observations is reasonable although some of the residuals

![Figure 6. Monthly mean above-baseline HFC-152a events observed in Europe and Australia 1994–2004. Data for Zeppelin and Cape Grim, plotted on the right y axis, are of a smaller scale than the left axis and offset for clarity.](image-url)
are slightly larger than the standard errors in the monthly means, shown in Figure 7.

### 3.2.2. Historical and Future Global HFC-152a Emissions Based on Consumption Compared With AGAGE Derived Global Emission Estimates

[24] Prompt emissions of HFC-152a from use in aerosol propulsion (mainly sprays used in technical applications), open cell foam blowing and one-component foam packs far outweigh other uses of this chemical. HFC-152a also has minor usage in some refrigeration applications in which it is retained in the system. Since there are few significant producers of HFC-152a, there are no data on production and consumption but the emissions reported to UNFCCC [United Nations Framework Convention on Climate Change (UNFCCC), 2005] by EU-15 member states match the confidential database maintained for regulators by EU-15 industry (Conseil Européen des Federations de l’Industrie Chimique (Cefic), personal communication, 2004). These data show that over 80% of emissions of HFC-152a in the EU-15 come from prompt categories and that their growth is linear. There are significant emissions from use of HFC-152a as replacement of VOCs in aerosol sprays in the U.S.A. but these are not reported explicitly to UNFCCC, even though most of the global emissions of HFC-152a occur in the U.S.A.

[25] Notwithstanding that production data for HFC-152a will not be published for confidentiality reasons, an historical and projected global emission estimate of HFC-152a has been compiled by Ashford and coworkers [Ashford et al., 2004a, 2004b]. Their methodology is summarized here. The group used a 2-point estimate for HFC-152a atmospheric concentration reported to the WMO (1.3 pmol/mol (ppt) in 1998 and 1.7 pmol/mol in 2000) as an anchor.

<table>
<thead>
<tr>
<th>Year</th>
<th>HFC-152a Global Emission, tonnes/yr</th>
<th>+ Error, tonnes/yr</th>
<th>- Error, tonnes/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995</td>
<td>7050</td>
<td>1590</td>
<td>1680</td>
</tr>
<tr>
<td>1996</td>
<td>6920</td>
<td>830</td>
<td>810</td>
</tr>
<tr>
<td>1997</td>
<td>8040</td>
<td>1020</td>
<td>1030</td>
</tr>
<tr>
<td>1998</td>
<td>13330</td>
<td>2340</td>
<td>2250</td>
</tr>
<tr>
<td>1999</td>
<td>9390</td>
<td>1280</td>
<td>1520</td>
</tr>
<tr>
<td>2000</td>
<td>16400</td>
<td>2350</td>
<td>2320</td>
</tr>
<tr>
<td>2001</td>
<td>14980</td>
<td>2190</td>
<td>2030</td>
</tr>
<tr>
<td>2002</td>
<td>21450</td>
<td>2870</td>
<td>2780</td>
</tr>
<tr>
<td>2003</td>
<td>23590</td>
<td>3250</td>
<td>3060</td>
</tr>
<tr>
<td>2004</td>
<td>28540</td>
<td>4170</td>
<td>4020</td>
</tr>
</tbody>
</table>

**Table 2.** Global Emission Estimates for HFC-152a Derived From the AGAGE 12-Box Model

**Figure 7.** Differences between the calculated 2-D model mole fractions using the annualized optimal emissions and the AGAGE monthly observations. These residuals (model minus observations) are compared to the standard deviations (vertical bars) in the observed monthly means.
These points have been fitted with a mathematical function which models the historical and anticipated consumption for other HFC and HCFC species for use in the foam-blowing and refrigeration sectors, similar to the mathematical function of emission has been fitted to derive the HFC-152a emissions. The agreement between the observations for HFC-134a (AGAGE data) and the modeled observations derived from the bottom-up model of Ashford et al. [2004a] is excellent. The agreement between AGAGE observations and modeled observations in Ashford et al. [2004a] is less good for HCFC-22 but is within the uncertainty limits of 7.4% (2 S.D. units). Such agreements for HFC-134a and HCFC-22 lends confidence to the comparisons reported here between the emission estimates derived from the AGAGE 12-box model of HFC-152a global emissions and those historical and projected global emission estimates from Ashford et al. [2004a, 2004b], shown in Figure 8.

The agreement between the AGAGE 12-box and the Ashford consumption model global emission estimate methods for HFC-152a is quite good. Given that the AGAGE 12-box model uses OH seasonality and that the Ashford estimates are primarily based on foam-blowing application historical and anticipated use (and calibrated by only two reference points from HFC-152a observations in 1998 and 2000), a difference of the order of 15–30% can be taken to indicate that both the observations and anticipated global emissions are in agreement within both methods' inherent uncertainties. The slope of the AGAGE derived emission estimates 1995–2004 is larger than that from Ashford et al. [2004b] which indicates a potentially larger historical global emission of HFC-152a than modeled by Ashford et al. [2004b]. It must be noted that the consumption approach only works well if there are several years of measurements and there are a sufficient number of adjustable parameters in the release model (which has not been the case hitherto with the Ashford model). Therefore we would have greater confidence that the rate of change in global emissions derived from the observation record with time would currently be a more accurate reflection of global HFC-152a emissions than those projected from the consumption model.

3.3. Regional Emission Estimates for HFC-152a Deduced From Above Baseline Elevations in the in Situ Observations and From a Consumption Model

3.3.1. European HFC-152a Emission Estimates

Three methods have been used to derive emission estimates of HFC-152a from European atmospheric observations. In addition, a top-down estimate of European HFC-152a emissions has been derived from the consumption model of Ashford et al. [2004b] for comparison. Each method has been described fully in previous publications and readers are referred to these reports for a detailed discussion on the methodology, assumptions and limitations of each model approach. The important assumptions of each model are included here to aid in the interpretation of the data.

The AGAGE method [Reimann et al., 2005], uses the AGAGE filter algorithm to define the baseline and above-baseline events for the Mace Head data set only. After subtraction of the baseline from the concurrent HFC-152a and CO Mace Head measurements, the method generates a ratio of average above-baseline HFC-152a to average above-baseline CO for each year of observation. The annual ratios were converted from volume to mass by multiplying by the respective molecular weights. Then the HFC-152a emissions for the EU-15 region were estimated by multiplying the HFC-152a/CO mass ratio by the reported CO annual emissions for the EU-15 region [Vestreng et al., 2005]. Results are shown in Table 3, method 1. This method assumes colocated sources, in time and space, of European emissions of HFC-152a and CO, a lack of distortion due to local sources and a negligible biogenic CO contribution (from biomass burning). Although the colocation of sources as the basic assumption of the tracer-ratio method criterion...
is not strictly met, it is reasonable to presume that both HFC 152a and CO emissions are caused by many diffuse, spatially similar anthropogenic sources. However, the accuracy of the estimates decreases for distant regions and underestimation of strong but remote point sources is possible if high emissions of CO are picked up during transport. The use of annual ratios of CO and HFC 152a during pollution events ensures that estimates are approximately representative of average conditions over Europe. Furthermore, the pollution events were filtered only by elevated concentrations in HFC 152a (instead of using CO) in order to assess the error of the tracer-ratio method. In this approach, HFC 152a point sources of limited duration (such as accidental release) could lead to significant overestimation of annual emissions and for a 2-year average were in fact up to 15% higher, which is taken as a cant overestimation of annual emissions and for a 2-year duration (such as accidental release) could lead to significant overestimation of annual emissions and for a 2-year average were in fact up to 15% higher, which is taken as a measure for the uncertainty (Table 3).

Table 3. European Emission Estimates for HFC-152a Based on Three Baseline Filtering Methods and a Consumption Method

<table>
<thead>
<tr>
<th>Year</th>
<th>Method 1: AGAGE Filter CO Ratio (Mace Head)</th>
<th>Method 2: NAME Inversion (Mace Head)</th>
<th>Method 3: EMPA Filter CO Ratio (Jungfraujoch)</th>
<th>Method 4: Consumption Based Estimate (EU-15) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992–1993</td>
<td>300 (±45)</td>
<td>470 (±10)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>1993–1994</td>
<td>350 (±53)</td>
<td>540 (±20)</td>
<td>40</td>
<td>120</td>
</tr>
<tr>
<td>1994–1995</td>
<td>450 (±68)</td>
<td>770 (±40, -60)</td>
<td>490</td>
<td>360</td>
</tr>
<tr>
<td>1995–1996</td>
<td>600 (±90)</td>
<td>950 (±40, -50)</td>
<td>1000</td>
<td>1780</td>
</tr>
<tr>
<td>1996–1997</td>
<td>800 (±120)</td>
<td>1230 (±60, -100)</td>
<td>1000</td>
<td>1780</td>
</tr>
<tr>
<td>1997–1998</td>
<td>950 (±143)</td>
<td>2010 (±80, -100)</td>
<td>1780</td>
<td>1780</td>
</tr>
<tr>
<td>1998–1999</td>
<td>1150 (±173)</td>
<td>2140 (±60, -40)</td>
<td>2130</td>
<td>2130</td>
</tr>
<tr>
<td>1999–2000</td>
<td>1350 (±203)</td>
<td>2040 (±70, -90)</td>
<td>2070</td>
<td>2070</td>
</tr>
</tbody>
</table>

*Error estimate ± 15%, see text for details.

For CFCs and HCFCs, manufacturers and importers are required to supply details of their sales within the EU to the Commission [European Union, 1999]. Although these data are confidential and cannot themselves be reported, they were made available through Cefic to assist with emissions calculations. The data are grouped into emission categories: prompt, including aerosol propellants and solvents; medium term, including refrigeration and air conditioning; and long term, including closed cell foam blowing. The consumption method is based on applying an emission function for HFC-152a in its major applications to Cefic reported data. The emission function is derived using the methods reported by Ashford et al. [2004a, 2004b] and System for Observation of Halogenated Greenhouse Gases in Europe [2004]. Estimated European (EU-15) emissions of HFC-152a from the consumption method are presented in Table 3, method 4. The uncertainty in the consumption emission estimates arises from the independent uncertainties in production estimates (small, less than 5%), assignment of this to end uses (small, less than 5%), emission rates from these uses (large, over 20%) and timing of these emissions (large, over 20%). Given the expected range of uncertainties in production and emission rates and the timing of emissions, the error in emissions calculated from consumption is expected to be similar to that calculated from global atmospheric measurements (i.e., about 15%, the range quoted in Table 3, method 4).

The NAME emission estimates cannot be derived for single years alone, but instead are derived as 2-year averaged emissions. For comparison purposes in Table 3, the data from the other 3 methods are also presented as the 2-year averaged emissions (in tonne/year) for the period...
shown. Most notable is the higher emission total derived using the EMPA model with Jungfraujoch data. The difference is partly explained by the fact that Jungfraujoch observes a different geographical area than Mace Head. Using Mace Head data, the Italian area is not solvable, Italian emissions will partially be reflected as edge effects in the emission totals for France and Germany whereas Jungfraujoch data will clearly distinguish these 3 geographical regions. Conversely Mace Head data can better distinguish United Kingdom and Ireland emissions compared to Jungfraujoch data. In addition, the AGAGE CO correlation method typically gives a lower emission estimate than that derived by NAME by an approximate factor of 2 [Reimann et al., 2005] which is within the uncertainty of the 3 observation-derived emission estimates presented here. There is broad agreement between the 3 observation-derived HFC-152a emission estimates and those of the consumption model. All four methods demonstrate that emission of HFC-152a from Europe has grown rapidly from 1998 to 2002 (over 50%/yr on average across all methods), and appears to have slowed since then (average 15%/yr for 2003–2004). The range of emission estimates for 2004 is 1,500–4,000 tonnes, implying a European fraction of about 5–15% of the 2004 HFC-152a global estimate (28,000 tonnes).

### 3.3.2. Australian Emission Estimates for HFC-152a

[35] The process of estimating Melbourne emissions involved first identifying pollution episodes in the Cape Grim record that were attributed to air masses that passed over the Melbourne region before traveling across Bass Strait to Cape Grim. Urban pollution markers (CFC-12, HCFC-141b (foam-blowing use) for comparison purposes [Dunse, 2002]). The amount of emission of HFC-152a is substantially less than the other replacement compounds. The magnitude of the error bar estimates demonstrate that the methodology is close to the limit of detection for HFC-152a emission estimation. There is no appreciable trend in HFC-152a emissions from Melbourne. Australian emission totals for similar compounds are of the order of 5 times those from Melbourne, which makes the total Australian HFC-152a emission estimate 5–10 tonnes per year. Relative to the global estimate of some 28,000 tonnes per annum in 2004, Australian HFC-152a emissions are negligible at less than 0.05% of the global total.

### 3.4. Regional Source Allocations for HFC-152a Emissions Based on Back Trajectory Modeling

[36] Emission maps derived from NAME inversion modeling of the Mace Head in situ observations for HFC-152a are shown in Figure 9. The emission maps indicate potential source regions of each release of HFC-152a and also indicate that the levels of pollution have risen from the periods 1995–1996 to 2001–2004. The NAME modeled Mace Head data indicates the dominant source of European HFC-152a emissions are from Germany, with lower contributions from France and the United Kingdom. While the total emission strength has grown since 1998–2004, the spread of source regions has remained largely unchanged from that reported by Ryall et al. [2001] for 1996–1998. However, there are regions of Europe (mainly southern and eastern Europe) which cannot be adequately represented by using Mace Head observations alone. Country-specific emissions are presented in Table 5 derived from the NAME inversion. The category “other” represents regions (e.g., Denmark, Sweden, Poland, Czech Republic, Spain, oceans/seas, etc.) which have not been specifically categorized.

[37] For comparison, the European geographic distribution of HFC-152a emissions derived using the consumption method for 2000 is presented in Table 6. Total European emissions were distributed among countries within Europe using the same distribution as the national emissions reported under the Rio Convention [UNFCCC, 2005]. Absolute values of the national emissions calculated by fractionation of the total European emission to a national level are some 30 to 40% higher than the equivalent figures submitted to UNFCCC. This is consistent with the reliance of the latter on country studies to estimate emissions by “bottom-up” calculations in which there are several sources of systematic error, such as the use of emissions under test (laboratory) conditions rather than in the field. The magnitude of the emission estimate for Europe is similar between the NAME inversion and the consumption method, but there are obvious differences in the spatial distribution, particularly notable for France and to a lesser extent the UK.

### Table 4. Melbourne Emissions of HFC-152a and Other Replacement Halocarbons Derived From Cape Grim Observations

<table>
<thead>
<tr>
<th>Year</th>
<th>HFC-152a</th>
<th>HFC-134a</th>
<th>HCFC-141b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1998</td>
<td>1 ± 1</td>
<td>38 ± 14</td>
<td>19 ± 7</td>
</tr>
<tr>
<td>1999</td>
<td>2 ± 1</td>
<td>59 ± 21</td>
<td>20 ± 7</td>
</tr>
<tr>
<td>2000</td>
<td>2 ± 1</td>
<td>84 ± 27</td>
<td>16 ± 6</td>
</tr>
<tr>
<td>2001</td>
<td>2 ± 1</td>
<td>65 ± 23</td>
<td>16 ± 6</td>
</tr>
<tr>
<td>2002</td>
<td>2 ± 1</td>
<td>70 ± 25</td>
<td>14 ± 5</td>
</tr>
<tr>
<td>2003</td>
<td>1 ± 1</td>
<td>113 ± 46</td>
<td>21 ± 9</td>
</tr>
<tr>
<td>2004</td>
<td>2 ± 1</td>
<td>73 ± 33</td>
<td>16 ± 8</td>
</tr>
</tbody>
</table>

a Unit is tonnes/yr.
Figure 9. Two-year HFC-152a emission maps derived from NAME modeling of Mace Head in situ observations, 1995–2004. Legend has been scaled by 1.0E12 for clarity.
coupled with very low occurrence of above-baseline deviation has little influence when included in the trajectory combination approach. The trajectory information for the other three European sites, derived from the EMPA MeteoSwiss modeling of above-baseline HFC-152a observations at individual monitoring sites is shown in Figure 10. The figures show yearly aggregated potential emission regions modeled from a combination of 48 hour back trajectories and concentrations above the background at the station, measured at the arrival time of the respective trajectory [Reimann et al., 2004].

In Figures 10a–10c distributions of sources of HFC-152a related to the observations at Jungfraujoch are shown, which indicate that the spread of emission regions is focused on northern Italy in 2002–2004, with a lesser influence from Germany and eastern Europe. This is in contrast to a previous emission source allocation [Reimann et al., 2004] which indicated a predominant German source for HFC-152a for the combined period 2000–2002, and represents a significant shift in the regional emission pattern over Europe. Similarly, the distributions derived from the Italian site at Monte Cimone (Figures 10d–10f) show an increase in source strength from 2002 to 2004, with the distribution again focused on northern Italy and to a lesser extent southern and central Germany. An analysis of the Mace Head observations using the Meteoswiss model is shown in Figures 10g–10i for 2002–2004, which concurs with the NAME model distribution of a dominant German source for HFC-152a. Italian source emissions are diluted and comixed with the German emissions such that Italian sources cannot be as represented adequately from the Mace Head observation record alone.

The regional emissions observed at Cape Grim are geographically limited given that the likely emission sources of an anthropogenic halocarbon will be from the major population centers. The sampling site is located in northeastern Tasmania, and so elevations detected in the baseline are almost exclusively from the Melbourne area. Further constraints on the geographical distribution of Australian source regions for HFC-152a (and other CFC replacement compounds) would require extra observation sites.

### 4. Conclusions

Mixing ratios of HFC-152a (CH$_3$CHF$_2$) have been observed at AGAGE stations in Europe and Australia for a 10-year period 1994–2004. Observational capacity has been increased in Europe by the SOGE sites since 2000. The segregation of data into baseline and above-baseline events has allowed the deduction of the long-term growth rate of HFC-152a. The 1994–2004 Northern Hemisphere baseline growth rate has been approximately 14%/yr, with a slight acceleration from 2000 to 2004. The average NH baseline for HFC-152a was ~5 ppt in 2004. The Southern Hemisphere average growth rate from 1998 to 2004 was 13%/yr and the mixing ratio was ~1.8 ppt in 2004. The amplitudes of the cycles in HFC-152a, deduced at all 5 monitoring sites are consistent with reaction of HFC-152a with the OH radical being the dominant removal mechanism although the cycle will be also influenced by year-to-year global emission variability and meteorological variations. A strong latitudinal gradient is implied from the observation that tropical air masses advected into Europe from southerly latitudes shows marked depletion in HFC-152a by up to 10–15% below the European baseline. The baseline observations from Mace Head and Cape Grim were used to estimate historical global emission estimates for HFC-152a. The 2-D model estimates highlight an approximately five-fold increase in global HFC-152a emissions from 1995 to 2004 and are in general agreement with previous reported

### Table 6. Distribution of European 2000 HFC-152a Emissions Derived From the Consumption Method [After Ashford et al., 2004a, 2004b]

<table>
<thead>
<tr>
<th>Country</th>
<th>2000 HFC-152a Emission Estimate, tonnes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>0</td>
</tr>
<tr>
<td>Belgium</td>
<td>12</td>
</tr>
<tr>
<td>Denmark</td>
<td>6</td>
</tr>
<tr>
<td>Finland</td>
<td>30</td>
</tr>
<tr>
<td>France</td>
<td>1</td>
</tr>
<tr>
<td>Germany</td>
<td>1292</td>
</tr>
<tr>
<td>Greece</td>
<td>4</td>
</tr>
<tr>
<td>Ireland</td>
<td>12</td>
</tr>
<tr>
<td>Italy</td>
<td>0</td>
</tr>
<tr>
<td>Luxembourg</td>
<td>2</td>
</tr>
<tr>
<td>Netherlands</td>
<td>11</td>
</tr>
<tr>
<td>Portugal</td>
<td>22</td>
</tr>
<tr>
<td>Spain</td>
<td>0</td>
</tr>
<tr>
<td>Sweden</td>
<td>2</td>
</tr>
<tr>
<td>UK</td>
<td>19</td>
</tr>
<tr>
<td>Total</td>
<td>1413</td>
</tr>
</tbody>
</table>

Standard error of distribution: %

**D06308**

GREALLY ET AL.: HFC-152a OBSERVATION AND EMISSIONS 1994–2004

**D06308**

Regional Breakdown of HFC-152a Emission Estimates for Europe Based on Total Emission Derived From Mace Head Observations by the NAME Inversion Model Shown in Table 3*

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ireland</td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>7</td>
<td>11</td>
<td>9</td>
<td>60</td>
</tr>
<tr>
<td>UK coastal</td>
<td>33</td>
<td>32</td>
<td>33</td>
<td>46</td>
<td>82</td>
<td>68</td>
<td>124</td>
<td>135</td>
<td>98</td>
<td>15</td>
</tr>
<tr>
<td>France</td>
<td>110</td>
<td>120</td>
<td>140</td>
<td>30</td>
<td>30</td>
<td>200</td>
<td>80</td>
<td>430</td>
<td>610</td>
<td>58</td>
</tr>
<tr>
<td>Germany</td>
<td>120</td>
<td>180</td>
<td>330</td>
<td>330</td>
<td>380</td>
<td>1360</td>
<td>1190</td>
<td>870</td>
<td>840</td>
<td>39</td>
</tr>
<tr>
<td>Benelux</td>
<td>39</td>
<td>5</td>
<td>21</td>
<td>85</td>
<td>60</td>
<td>13</td>
<td>87</td>
<td>71</td>
<td>81</td>
<td>77</td>
</tr>
<tr>
<td>Other</td>
<td>163</td>
<td>199</td>
<td>244</td>
<td>455</td>
<td>674</td>
<td>364</td>
<td>627</td>
<td>523</td>
<td>852</td>
<td></td>
</tr>
<tr>
<td>Europe</td>
<td>470</td>
<td>540</td>
<td>770</td>
<td>950</td>
<td>1230</td>
<td>2010</td>
<td>2140</td>
<td>2040</td>
<td>2490</td>
<td>8</td>
</tr>
</tbody>
</table>

*Units in tonnes.

**Percent variability of the maximum emission solution difference about the mean emission solution.

Belgium, Netherlands, Luxembourg.
Figure 10. EMPA trajectory modeling of (a–c) Jungfraujoch (2002–2004), (d–f) Monte Cimone (2002–2004), and (g–i) Mace Head (2002–2004) indicating the distribution of HFC-152a above-baseline events for each observation station. The scale and color contour is relative to the lowest occurrence of likely source region trajectories (green) to the highest occurrence of trajectory (brown).
emissions derived from a consumption model. The AGAGE derived emissions show a larger slope than the consumption model, which potentially indicates that more rapid emission of HFC-152a can be deduced from observational data than previously estimated by consumption methods. The most recent estimate for global HFC-152a emissions is 28,000 tonnes in 2004. Regional HFC-152a emission estimates from Europe have been calculated based on both the in situ observations and on a consumption model. The specific model results vary but show that the European emission of HFC-152a has increased rapidly from the range of 300–500 tonnes/yr in 1995–1996 to the range of 1,500–4,000 tonnes/yr in 2004. The European contribution to the global HFC-152a emissions is in the range 5–15%. Australian HFC-152a emissions have been constant from 1998 to 2004, with estimated emissions of 5–10 tonnes/yr contributing less than 0.05% of the global total. Regional source allocation of European HFC-152a emissions based on trajectory maps indicate the dominance of German sources and increasingly of Italian sources, with lower contributions from France, the United Kingdom and other regions. Derived Australian regional emissions are distributed on the Melbourne area, although this cannot be refined further using data from only one observational site.

[41] Acknowledgments. We gratefully acknowledge the cooperation and efforts of the station operators and support staff at all five monitoring stations. We also thank the Physics Department, National University of Ireland, Dublin, for making the research facilities at Mace Head available. The operation of the AGAGE stations was supported by NASA (grants NAGW-732, NAGI-1805, and NAG5-3974 NAG-12099 to MIT and grants NAGW-2034 and NAGS-4023 to SIO), the Department of the Environment, Food and Rural Affairs (UK) (contracts PEC 1/1/130 and 7/10/154, EP1 1/1/82 and EP1 1/130 to International Science Consultants, and CPEG 27 to the UK Meteorological Office), the Commonwealth Scientific and Industrial Research Organization (CSIRO Australia), Bureau of Meteorology (Australia), and the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS). The operation of SOGE stations was supported by the EU Commission of the European Communities Research Directorate – General 5th Framework Programme (EU FP-5) theme of Energy, Environment and Sustainable Development (project EUVK-2000-00674). Financial support for the Jungfranjoech measurements is acknowledged from the Swiss National Program HALCLIM (Swiss Agency of Environment, Forests and Landscape, SAEFL, BUWAL).

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18 of 18