Global trends, seasonal cycles, and European emissions of dichloromethane, trichloroethene, and tetrachloroethene from the AGAGE observations at Mace Head, Ireland, and Cape Grim, Tasmania

P. G. Simmonds,1 A. J. Manning,2 D. M. Cunnold,3 A. McCulloch,1 S. O’Doherty,1 R. G. Derwent,4 P. B. Krummel,5 P. J. Fraser,5 B. Dunse,5 L. W. Porter,6 R. H. J. Wang,3 B. R. Greally,1 B. R. Miller,7 P. Salameh,7 R. F. Weiss,7 and R. G. Prinn8

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[1] In situ observations (every 4 hours) of dichloromethane (CH2Cl2) from April 1995 to December 2004 and trichloroethene (C2HCl3) and tetrachloroethene (C2Cl4) from September 2000 to December 2004 are reported for the Advanced Global Atmospheric Gases Experiment (AGAGE) station at Mace Head, Ireland. At a second AGAGE station at Cape Grim, Tasmania, CH2Cl2 and C2Cl4 data collection commenced in 1998 and 2000, respectively. C2HCl3 is below the limit of detection at Cape Grim except during pollution episodes. At Mace Head CH2Cl2 shows a downward trend from 1995 to 2004 of 0.7 ± 0.2 ppt yr−1 (ppt: expressed as dry mole fractions in 10−12), although from 1998 to 2004 the decrease has been only 0.3 ± 0.1 ppt yr−1. Conversely, there has been a small but significant growth of 0.05 ± 0.01 ppt yr−1 in CH2Cl2 at Cape Grim. The time series for C2HCl3 and C2Cl4 are relatively short for accurate trend analyses; however, we observe a small but significant decline in C2Cl4 (0.18 ± 0.05 ppt yr−1) at Mace Head. European emissions inferred from AGAGE measurements are compared to recent estimates from industry data and show general agreement for C2HCl3. Emissions estimated from observations are lower than industry emission estimates for C2Cl4 and much lower in the case of CH2Cl2. A study of wildfires in Tasmania, uncontaminated by urban emissions, suggests that the biomass burning source of CH2Cl2 may have been previously overestimated. All three solvents have distinct annual cycles, with the phases and amplitudes reflecting their different chemical reactivity with OH as the primary sink.


1. Introduction

[2] Chlorinated hydrocarbons are emitted to the atmosphere from their widespread use as solvents in diverse industrial, commercial and domestic applications. The major chlorinated solvents controlled by the Montreal Protocol and its amendments are methyl chloroform (CH3CCl3) and carbon tetrachloride (CCl4). Dichloromethane (CH2Cl2), trichloroethene, (C2HCl3) and tetrachloroethene (C2Cl4) are three important chlorinated solvents that are not regulated by the Montreal Protocol, because of their low impacts on stratospheric ozone as a consequence of their short atmospheric lifetimes. However, they are classed as hazardous air pollutants and toxic volatile organic compounds in regional air quality inventories.

[3] About 70% of CH2Cl2 emissions are anthropogenic in origin from foam plastic products, metal cleaning and other solvent uses [Cox et al., 2003]. Estimated industrial emissions from audited sales data were about 580 Gg in 1990, and have declined steadily since then at about 12 Gg yr−1 [McCulloch et al., 1999]. The nature and magnitude of natural CH2Cl2 sources are very uncertain. Natural sources include the ocean [Keene et al., 1999; Khalil, 1999] with estimated emissions of 190 Gg yr−1. Lober et al. [1999] estimated emissions due to biomass burning of about 60 Gg yr−1. The major atmospheric removal process for CH2Cl2 is destruction...
by OH with a resultant atmospheric lifetime of 5–6 months [Ko and Poulet, 2003]. Graedel and Keene [1996] estimate that about 2% of CH₂Cl₂ emissions reach the stratosphere. Measurements near the tropical tropopause in 1992 averaged 14.9 ± 1.1 ppt [Schaufler et al., 1993].

[4] The atmospheric history of CH₂Cl₂ reconstructed from the analysis of Antarctic firn air shows a steep increase in concentration from about 1960, peaking in 1990, and then a decrease. The firn record suggests significantly lower emissions due to the oceans than the estimates by Khalil [1999], and an enhanced terrestrial source [Trudinger et al., 2004]. Southern Hemisphere CH₂Cl₂ levels in the pre-1940s were 1–2 ppt, 15–20% of peak levels in the 1980s–1990s, suggesting natural emissions are less than 20% of peak emissions. Tropospheric mixing ratios of 15–45 ppt in 0–45°N and 15–20 ppt in 30–0°S were obtained in an ocean cruise in the Atlantic during August/September 1989 [Koppmann et al., 1993]. Butler et al. [1998], Elkins et al. [2001] reported 1995–1997 mixing ratios of approximately 20–40 ppt at Niwot Ridge, with 20% larger values at higher northern latitudes (e.g., Barrow), and significantly lower values (8–12 ppt) in the Southern Hemisphere (SH). The average background concentration observed at Cape Grim, Tasmania during 1998–2000 was 8.9 ± 0.2 ppt [Cox et al., 2003]. Measurements near the tropical troposphere in 1992 averaged 15 ± 1 ppt [Schaufler et al., 1993].

[5] Trichloroethene is mainly used as a degreasing solvent with OH destruction as its major atmospheric sink, resulting in an atmospheric lifetime of just 4–7 days; in addition C₂HCl₃ can also undergo reductive dechlorination to 1, 2-dichloroethylene through the activity of soil microbes [Kloepfer et al., 1985]. For longer-lived gases transport will result in the gas seeing a globally averaged OH, but this is not true for this gas. Global emissions have remained relatively constant from 1988 to 1996 at about 240 Gg yr⁻¹ [McCulloch et al., 1999]. There are reported natural sources of C₂HCl₃ and C₂Cl₂H from the oceans and seawater algae [Abrahamsson et al., 1995; Khalil, 1999]. Recently, it has been reported that salt lakes are a natural source of both C₂HCl₃ and C₂Cl₂H due to the microbial activity of halobacteria [Weissflog et al., 2005].

[6] Estimated tropospheric mixing values for C₂HCl₃ in the Northern Hemisphere (NH) are 1–5 ppt and 0.01–0.1 ppt in the SH, contributing to an annually averaged atmospheric burden of 3.1–5.3 Gg [Ko and Poulet, 2003]. Koppmann et al. [1993] measured NH mixing ratios of 3 ± 1 ppt in 1989. Average baseline concentrations observed at Ny Ålesund, Spitzbergen, (78°N, 11°E) during the summer of 1997 were 0.12 ± 0.03 ppt, and during the CHAOS cruise in 1998; C₂HCl₃ concentrations were 1.58 ± 0.45 for the remote Atlantic and Arctic oceans [Dimmer et al., 2001]. Yokouchi et al. [1996] reported measurements at Alert, Canada (1992–1994) from 0.01 ppt in summer to about 8 ppt in winter.

[7] Tetrachloroethene is used primarily as a surface degreasing agent and a dry cleaning fluid. Small, but significant quantities, of C₂Cl₄ are emitted in the flue gas from coal-fired power plants [Garcia et al., 1992]. McCulloch et al. [1999] reported global emissions during 1990 of 366 Gg, which have declined over the period 1988–1996 at about 23 Gg yr⁻¹. Emissions from coal-fired power plants are estimated to be only 19 Gg yr⁻¹. The atmospheric lifetime of C₂Cl₄ is 3–4 months resulting from its primary atmospheric sink-reaction with OH [Olaguer, 2002]. Rudolph et al. [1996] noted that C₂Cl₄ reacts about 300 times faster with Cl atoms than with OH, although tropospheric levels of Cl are too small for this to be a significant sink. Simpson et al. [2003] have suggested that C₂Cl₄ undergoes cirrus-activated depletion in the upper troposphere. Oxidation of tropospheric C₂Cl₄ by OH yields phosgene (COCl₂) as the primary product [Franklin, 1994]. It has also been estimated that about 5% of C₂Cl₄ released into the atmosphere is converted into trichloroacetic acid (CCl₃COOH, TCA), via an alternate pathway involving Cl atoms [Franklin and Sidebottom, 1999; McCulloch, 2002].

[8] Average measurements of C₂Cl₄ in the remote marine boundary layer in 1989 were 13 ± 7 ppt in the NH and 2.7 ± 0.4 in the SH [Koppmann et al., 1993]. These values are similar to other measurements (21 ± 5 ppt from 30 to 90°N, 7 ± 3 from 0 to 30°N, and 2.2 ± 0.5 in the SH [Wiedmann et al., 1994]; 16 ± 7 ppt over the North Atlantic [Blake et al., 1996a]). Tetrachloroethene exhibits a strong interhemispheric gradient [Wang et al., 1995; Rudolph et al., 1996] with an estimated tropospheric mixing ratio of 5–15 ppt in the NH and 0.7–1.5 ppt in the SH [Ko and Poulet, 2003]. Dimmer et al. [2001] reported an average baseline concentration of 4.26 ± 0.84 ppt during the 1998 CHAOS cruise in the northeastern Atlantic and Arctic oceans (April–May 1998); during a separate field campaign (July–September 1997) at Ny Ålesund (Norwegian Arctic) much lower concentrations of 1.77 ± 0.07 ppt were observed. Approximately 1 year (March 1998 to January 1999) of high-frequency C₂Cl₄ and C₂HCl₃ measurements have been reported for the northeastern United States with clean background C₂Cl₄ and C₂HCl₃ levels around 2 and 3 ppt respectively and polluted levels up to 90 and 140 ppt respectively; surface emissions have been estimated from the data during pollution events [Kleiman and Prinn, 2000]. From 1994 to 1997, Hurst et al. [1998] reported a downward trend in C₂Cl₄ of approximately 0.63 ppt yr⁻¹ from selected nighttime measurements on a North Carolina tower. On the basis of a 14-year record of flask measurements, Simpson et al. [2004] determined that the annual global C₂Cl₄ mixing ratio was 6.3 ± 0.6 ppt in 1989, which declined to 3.5 ± 0.2 ppt by 2002, indicating that the global C₂Cl₄ burden decreased by about 205 Gg over the same period. However, Barnes et al. [2003] noted average emissions of C₂Cl₄ of 0.32 kg/person with no uniform trend from 1996 to 1998 for the New York City-Washington D.C., corridor.

[9] Flask-sampling programs have provided a long-term record of the temporal and spatial distribution of these three chlorinated compounds [Gautrois et al., 2003; Blake et al., 2003; Thompson et al., 2004; Simpson et al., 2004]. However, high-frequency measurements of these species are relatively limited. High-frequency data are valuable as they allow estimates of regional emissions [Kleiman and Prinn, 2000; Manning et al., 2003] and better estimates of annual cycles and trends. Here, we report in situ gas chromatographic-mass spectrometric observations of CH₂Cl₂, C₂HCl₃, and C₂Cl₄ from the Mace Head, Ireland, and Cape Grim, Tasmania, obtained as part of the AGAGE
Global annual emissions have been calculated from the baseline measurements and these are compared to recent estimates of emissions from audited production and sales data provided by industry; the latter suggest that there are no significant seasonal variabilities in the emissions [McCulloch and Midgley, 1996; McCulloch et al., 1999]. Estimates of European emissions have been calculated using the NAME (Numerical Atmospheric Dispersion Modeling Environment) Lagrangian particle model after identifying the pollution episodes in the Mace Head observations. The model classifies the origin of air masses arriving at Mace Head and the best fit algorithm (called simulated annealing) provides an improved ability to determine emission distributions from region to region [Manning et al., 2003].

2. Experimental Section
2.1. Instrumentation

An automated instrument for the analysis of atmospheric halocarbons was installed at Mace Head, Ireland, in October 1994, using an adsorption-desorption system (ADS) unit coupled to a Magnum ion trap GC-MS (Finnigan Instruments, Hemel Hempstead, UK) [Simmonds et al., 1995]. The Magnum instrument was replaced in October 1997 with a HP6890 GC coupled to a HP5973 MS (Agilent Ltd, U.K.). Both instruments were operated in parallel from October 1997 to January 1998, after which the Magnum instrument was retired from service. Calibrated measurements of CH$_2$Cl$_2$ have been recorded at Mace Head from 1995 to 2004. An identical ADS-GC-MS (Agilent) instrument was installed at the Cape Grim, Tasmania, in November 1997, with CH$_2$Cl$_2$ observations beginning in early 1998. Calibrated measurements of C$_2$HCl$_3$ only commenced at Mace Head in 1999, and C$_2$HCl$_3$ is not observed (below detection limit) at Cape Grim except in pollution episodes. Calibrated measurements of C$_2$Cl$_4$ commenced at both Mace Head and Cape Grim in 2000.

A full description of the instrument is given by Prinn et al. [2000] and Sturrock et al. [2001]. A brief summary of the automated GC-MS system is provided here. A nominal, precisely repeatable, two liters of ambient air or calibration standard are trapped onto a three-stage mixed composition trap system. The trapped sample is thermally desorbed to an ultimate temperature of 245°C for 3 min. The desorbed sample is then diluted 100:1, converted to an HClClF$_2$ mixture, and the resulting mixture is transferred to a microtrap (thermoelectric cooler), maintained at approximately −50°C during sampling. The microtrap is located between two in-line cooling systems and the temperature can be adjusted to maintain the sample at a constant temperature. The microtrap is interfaced to the benchtop GC-MS. The microtrap is located between two in-line cooling systems and the temperature can be adjusted to maintain the sample at a constant temperature. The microtrap is interfaced to the benchtop GC-MS.
are shown in black, while pollution events, identified by a statistical algorithm [O’Doherty et al., 2001; Cunnold et al., 2002], are shown in red. Overall there has been a decline in the magnitude of the pollution events since observations first began in 1995. This decline is seen more clearly in Figure 1b, where the baseline monthly means (with pollution events removed) have been subtracted from the monthly means including pollution. A 24-month moving average of the excess CH$_2$Cl$_2$ due to local/regional pollution (in ppt) shows a reduction of approximately 46% over the 10 years of observations. There is a substantial decrease in local/regional emissions after 1998, which then remain stable up to 2004.

Figure 2 shows the time series of baseline data (pollution episodes removed) for CH$_2$Cl$_2$, C$_2$HCl$_3$ and C$_2$Cl$_4$ observed at Mace Head. There is a 10–20% drop in the mixing ratios of CH$_2$Cl$_2$ after 1998 which would equate to a decrease in global emissions of approximately 50–100 Gg yr$^{-1}$. Figure 3 shows the comparable baseline time series for CH$_2$Cl$_2$ and C$_2$Cl$_4$ recorded at Cape Grim. The rapid decline in CH$_2$Cl$_2$ observed at Mace Head after 1998 is not observed at Cape Grim. Trichloroethene is not observed regularly at Cape Grim as concentrations are routinely below the detection limit, except in occasional pollution episodes.

### 4. Box Model Calculations

The AGAGE CH$_2$Cl$_2$, C$_2$HCl$_3$ and C$_2$Cl$_4$ observations have been fitted by an empirical model with linear, quadratic, and annual and semiannual harmonic terms. The results for CH$_2$Cl$_2$ are shown in Table 1.

\[
\chi(t) = a + b \left( \frac{N}{12} \right) P_1 \left( \frac{t}{N} - 1 \right) + \frac{1}{3} d \left( \frac{N}{12} \right)^2 P_2 \left( \frac{t}{N} - 1 \right) + c_1 \cos \left( \frac{2\pi t}{12} \right) + s_1 \sin \left( \frac{2\pi t}{12} \right) + c_2 \cos \left( \frac{4\pi t}{12} \right) + s_2 \sin \left( \frac{4\pi t}{12} \right)
\]

\[1\]

Table 1 lists the empirical model fits for each of the chlorinated solvents during the periods of the combined Magnum/Agilent-GC-MS measurements (1995–2004), and the Agilent GC-MS measurements alone (1998–2004). Here $P_i$ are the Legendre polynomials of order $i$, $t$ is the time measured in months, with zero being the first month of the analysis period, and $2N$ is the number of months of data analyzed. Note that the reported phases of the seasonal cycles all have 1 July as the zero phase points. The coefficients $a$ defines the average mole fraction, while coefficients $b$, $d$ define the linear trend and the acceleration in trend, respectively. The coefficients $c$ and $s$ define the annual cycle in concentration.

Table 2 compares the results from this work with other earlier observations reported in the literature.

### 4.1. Twelve-Box Model Results

Calculations have been made with the two-dimensional AGAGE 12-box model [Cunnold et al., 1994, 1997]. The model contains four semihemispheric equal mass boxes in each of three regions: 1000–500 mb (the lower troposphere), 500–200 mb (the upper troposphere)
and 200–0 mb (the stratosphere). Transport parameters are varied seasonally but not annually and they have been adjusted to match the observed baseline mean gradients and seasonal cycles for CFC-11 and CFC-12 at the AGAGE sites. Tropospheric OH values are also varied seasonally but not annually. The annual mean values are based on simulating the observed AGAGE measurements of methyl chloroform with the 12-box model [Prinn et al., 2005, and references therein]. The seasonal cycles of OH are based on the calculations of Spivakovsky et al. [2000]. Using reaction rates with OH from Sander and Friedl [2003], we obtain global lifetimes of CH$_2$Cl$_2$ and C$_2$Cl$_4$ equal to 154 and 98 days respectively. No calculations have been made with the 12-box model for C$_2$HCl$_3$ because its very short lifetime makes this inappropriate.

Annual global emission estimates, up to 2000, for the solvents have been made and compared against McCulloch and Midgley [1996] and McCulloch et al. [1999]. The spatial distributions of the anthropogenic emissions in the four semihemispheric regions in the year 2000 (and in 1990) are taken from the Global Emission Inventory Activity (GEIA) database described by McCulloch et al. [1999]. In 2000, this gives the emission proportion by semihemisphere from north to south of 0.828, 0.107, 0.065 and 0.000 for C$_2$Cl$_4$, and of 0.811, 0.117, 0.072, and 0.000 for CH$_2$Cl$_2$. The 12-box model has been used to estimate the global emissions annually which provide the best fit to the measured mole fractions at Mace Head and Cape Grim, [Cunnold et al., 1994, 1997]. For the very short lived gases however, the best fit is determined by minimizing the percentage differences from the individual means at the two sites. For C$_2$Cl$_4$ over the period 1999 to 2003 the estimated emissions range from 250 Gg yr$^{-1}$ in 2000 to 205 Gg yr$^{-1}$ in 2002. The average annual emission is 228 Gg yr$^{-1}$ over this period, and may be compared against the industrially derived global emission estimates of 268 ± 27 Gg yr$^{-1}$ (two sigma) for 1999 and 2000 McCulloch et al. [1999] and they also calculate less than ±10% variation in the annual emissions before that as far back as 1992. The AGAGE measurements suggest that the emissions were lower after 2000 by approximately 15%. The model is calculating a mean difference between Mace Head and Cape Grim which is approximately 7% larger than that observed. The box model suggests that the ratio of NH to SH mole fractions in the lower troposphere is 4.5.

For CH$_2$Cl$_2$ the model over predicts the difference between Mace Head and Cape Grim observations for a purely anthropogenic source. A better fit to the observations is obtained by adding a 10% combined source contribution from the ocean and biomass burning. The model results do not support a 30% contribution from the combined ocean/biomass burning source primarily because the measurements at Cape Grim are then over predicted. On the basis of a 10% contribution the model matches the observed differences between Mace Head and Cape Grim to better than 5%. The box model then suggests the ratio of NH to SH mole fractions in the lower troposphere is 2.7. An alternative scenario which is more consistent with the observed gradient for a 30% contribution from natural sources (see section 1) is that the ocean source is smaller and there is a terrestrial source. The annual emission estimates from 1999 to 2003, calculated in the box model, are in the range 515 ± 22 Gg yr$^{-1}$ and the variations from year to year are not statistically significant at the 95% confidence level. From 1995 to 1997 the estimates are in the range 626 ± 11 Gg yr$^{-1}$. The change in annual emission

![Figure 1b. Decline in the magnitude of the CH$_2$Cl$_2$ pollution events at Mace Head, Ireland, from 1995 to 2004. Shown are the monthly means of the pollution events minus the baseline monthly means and the 24-month moving average (solid square line).](image-url)
estimates between the two periods is certainly statistically
significant. The anthropogenic contribution to the global
emission estimates in 1995 to 1997 fit the industry estimates
of McCulloch et al. [1999] provided that 15 ± 10% of the
emissions are nonanthropogenic. On the other hand for
1999/2000 the industry estimates would only fit the model-
derived global emission estimates if all the emissions were
anthropogenic.

4.2. Comparisons With Previous Measurements

[25] There are some significant differences when com-
paring the observed mixing ratios reported here with earlier
publications, as noted in Table 2. Because of the large
pollution events that occur much of the time in the Northern
Hemisphere (about 30% of the time at Mace Head, associ-
ated with air arriving from the direction of the European
continent) it is most useful to compare baseline values.
Unfortunately for many of the measurements against which
AGAGE measurements might be compared, the data have
not been filtered to remove pollution events. Therefore we
examine the agreement with the lower values during indi-
vidual months and values within 10% are considered good
agreement. Even for baseline concentrations there are sub-
stantial variations with latitude, primarily in 0–40°N [see,
e.g., Simpson et al., 2004] and with the time of year. The
12-box model is used to roughly adjust for spatial and
temporal differences relative to the time series observed at
Mace Head and Cape Grim. On average the model is
indicating an annual cycle phase at Mace Head, which is
just 2 weeks ahead of that observed. At Cape Grim the
model phase is only a week ahead of that observed.
However, the model currently under predicts the amplitude
of the seasonal cycles by up to a factor of two. Therefore the
corrections for the time of year are based on the amplitudes
of the measured annual cycles.

Figure 2. Baseline selected data (dots), best fit line (solid line) and trend line (shaded line) for CH$_2$Cl$_2$, C$_2$Cl$_4$ and C$_2$HCl$_3$ recorded at Mace Head, Ireland. Note that Magnum and Agilent GC-MS CH$_2$Cl$_2$
measurements have been combined with the Magnum mole fractions reduced by 5.78%.
Table 1. Empirical Model Fit (Equation (1)) to the Chlorinated Solvent Measurements at Mace Head and Cape Grim\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>Mean, ppt</th>
<th>Trend, ppt/yr</th>
<th>d, ppt/yr(^b)</th>
<th>c(_1), ppt</th>
<th>s(_1), ppt</th>
<th>c(_2), ppt</th>
<th>S(_2), ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)Cl</td>
<td>32.2 ± 0.4</td>
<td>-0.7 ± 0.2</td>
<td>0.2 ± 0.1</td>
<td>-1.5 ± 0.4</td>
<td>-5.3 ± 0.4</td>
<td>0.5 ± 0.4</td>
<td>-1.6 ± 0.4</td>
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<tr>
<td>Mace Head, in situ</td>
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<td>Jul 1995 to Dec 2004(^a)</td>
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<tr>
<td>Mace Head, in situ</td>
<td>30.8 ± 0.2</td>
<td>-0.3 ± 0.1</td>
<td>0.7 ± 0.1</td>
<td>-1.5 ± 0.3</td>
<td>-5.3 ± 0.3</td>
<td>0.3 ± 0.3</td>
<td>-1.4 ± 0.3</td>
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<tr>
<td>Jul 1998 to Dec 2004(^a)</td>
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<tr>
<td>Cape Grím, in situ</td>
<td>8.74 ± 0.02</td>
<td>0.05 ± 0.01</td>
<td>0.10 ± 0.02</td>
<td>0.80 ± 0.03</td>
<td>1.28 ± 0.03</td>
<td>-0.05 ± 0.03</td>
<td>-0.09 ± 0.03</td>
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<td>Jul 1998 to Dec 2004</td>
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<tr>
<td>CH(_2)Cl(_2)</td>
<td>1.14 ± 0.07</td>
<td>-0.01 ± 0.04</td>
<td>0.03 ± 0.06</td>
<td>-1.31 ± 0.10</td>
<td>-0.58 ± 0.10</td>
<td>0.32 ± 0.10</td>
<td>0.39 ± 0.10</td>
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<td>Mace Head, in situ</td>
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<td>Jul 1999 to Dec 2004</td>
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<tr>
<td>Cape Grím, in situ</td>
<td>N.D.</td>
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<tr>
<td>CH(_2)Cl(_3)</td>
<td>4.94 ± 0.06</td>
<td>-0.18 ± 0.05</td>
<td>0.11 ± 0.09</td>
<td>-1.41 ± 0.09</td>
<td>-1.51 ± 0.09</td>
<td>0.09 ± 0.09</td>
<td>-0.20 ± 0.09</td>
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<td>Mace Head, in situ</td>
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<tr>
<td>Cape Grím, in situ</td>
<td>0.75 ± 0.01</td>
<td>-0.01 ± 0.01</td>
<td>0.01 ± 0.02</td>
<td>0.22 ± 0.01</td>
<td>0.21 ± 0.02</td>
<td>-0.01 ± 0.02</td>
<td>0.00 ± 0.02</td>
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<tr>
<td>Jul 2000 to Dec 2004</td>
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\(^a\) Combined Magnum and Agilent GC-MS measurements (note that Magnum mole fractions have been reduced by 5.78%).
\(^b\) Combined Magnum and Agilent GC-MS measurements only. The error bars are based on the standard deviations of the residuals. Because the residuals typically do not have a white noise spectrum, the standard deviations have been increased (but never decreased) to reflect the shape of the power spectrum of the residuals.

Table 2. Comparison of Results Presented in the Work With Mixing Ratios and Trends of CH\(_2\)Cl\(_2\), C\(_2\)HCl\(_3\), and C\(_2\)Cl\(_4\) Reported in the Literature\(^c\)

<table>
<thead>
<tr>
<th>Mixing Ratio, ppt</th>
<th>NH</th>
<th>Year (Average)</th>
<th>Trend, ppt/yr</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)Cl</td>
<td>30.8 ± 0.2</td>
<td>(1998–2004)</td>
<td>-0.7 ± 0.2 (1995–2004), -0.3 ± 0.1 (1998–2004)</td>
<td>this work (Mace Head)</td>
</tr>
<tr>
<td>15–45 average 36 ± 6</td>
<td>8.74 ± 0.03</td>
<td>(1998–2004)</td>
<td>0.05 ± 0.01 (1998–2004)</td>
<td>this work (Cape Grím)</td>
</tr>
<tr>
<td>24.2–71.6</td>
<td>NM</td>
<td>1989</td>
<td>-4.0%(^c)/yr</td>
<td>Koppmann et al. [1993]</td>
</tr>
<tr>
<td>NM</td>
<td>8.9 ± 0.2</td>
<td>(1998–2000)</td>
<td>ND</td>
<td>Cox et al. [2003]</td>
</tr>
<tr>
<td>C(_2)HCl(_3)</td>
<td>1.14 ± 0.06</td>
<td>(1999–2004)</td>
<td>ND</td>
<td>this work</td>
</tr>
<tr>
<td>0.3–15</td>
<td>NM</td>
<td>1989</td>
<td>ND</td>
<td>Koppmann et al. [1993]</td>
</tr>
<tr>
<td>0.01–8</td>
<td>NM</td>
<td>(1992–1994)</td>
<td>ND</td>
<td>Yokouchi et al. [1996]</td>
</tr>
<tr>
<td>0.5–7.8</td>
<td>NM</td>
<td>(1989–1996)</td>
<td>-2.8%(^c)/yr</td>
<td>Gautrais et al. [2003]</td>
</tr>
<tr>
<td>1.58 ± 0.45</td>
<td>NM</td>
<td>1998</td>
<td>ND</td>
<td>Dimmer et al. [2001]</td>
</tr>
<tr>
<td>1–5</td>
<td>0.01–0.1</td>
<td>1992</td>
<td>ND</td>
<td>Ko and Poulet [2003]</td>
</tr>
<tr>
<td>C(_2)Cl(_4)</td>
<td>4.94 ± 0.06</td>
<td>(2000–2004)</td>
<td>-0.18 ± 0.05</td>
<td>this work (Mace Head)</td>
</tr>
<tr>
<td>0.75 ± 0.01</td>
<td>(2000–2004)</td>
<td>-0.01 ± 0.01</td>
<td>this work (Cape Grím)</td>
<td></td>
</tr>
<tr>
<td>13 ± 7</td>
<td>2.7 ± 0.4</td>
<td>1989</td>
<td>ND</td>
<td>Koppmann et al. [1993]</td>
</tr>
<tr>
<td>21 ± 5</td>
<td>2.2 ± 0.5</td>
<td>(1982–1989)</td>
<td>ND</td>
<td>Wiedmann et al. [1994]</td>
</tr>
<tr>
<td>2.7 ± 15.3</td>
<td>NM</td>
<td>(1989–1996)</td>
<td>-13.5%(^c)/yr</td>
<td>Gautrais et al. [2003]</td>
</tr>
<tr>
<td>16 ± 7</td>
<td>NM</td>
<td>1992</td>
<td>ND</td>
<td>Blake et al. [1996a], Hurst et al. [1998]</td>
</tr>
<tr>
<td>Highly variable</td>
<td>NM</td>
<td>(1994–1997)</td>
<td>-0.63 ± 0.38 (nighttime average)</td>
<td></td>
</tr>
<tr>
<td>4.26 ± 0.84</td>
<td>NM</td>
<td>1998</td>
<td>ND</td>
<td>Dimmer et al. [2001]</td>
</tr>
<tr>
<td>13.9 ± 0.5</td>
<td>2.1 ± 0.2</td>
<td>1989</td>
<td>-0.1 [1990]</td>
<td>Simpson et al. [2004]</td>
</tr>
<tr>
<td>6.5 ± 0.2</td>
<td>1.5 ± 0.1</td>
<td>2002</td>
<td>-0.4 [2002]</td>
<td>Simpson et al. [2004]</td>
</tr>
</tbody>
</table>

\(^c\) NM, not measured; ND, not determined.
in 1996–1998, either the Koppmann et al. [1993] measurement scale differed from the AGAGE scale by approximately 10% or the emissions were larger in 1989 than in 1996–1998 by approximately an additional 10%. The 12-box model suggests upper tropospheric mole fractions in 0–30°N of 22 ppt in 1992 but only 7 ppt values in the lower stratosphere in early 1992, it is therefore unclear whether there is inconsistency with the Schauffler et al. [1993] values of 14.9 ppt at the tropical tropopause at that time. There is good agreement with the Dimmer et al. [2001] baseline values in the Arctic in July/September 1997. Encouragingly there was a 15–20% decrease in the mixing ratios of CH$_2$Cl$_2$ observed at several of the NOAA NH monitoring sites from 1996 to 1999 which is in line with the approximately 20% decline in the Mace Head observations post 1998 [Thompson et al., 2004].

The AGAGE measurements give a global lower-tropospheric average for C$_2$Cl$_4$ in 2002 of 2.6 ppt. This is about 25% lower than the Simpson et al. [2004] UCI (University of California, Irvine) reported value of 3.5 ppt from their extensive sampling in the Pacific region. Using the McCulloch et al. [1999] emissions, which indicate that the emissions in 1989 were 58% larger than in 2000, and the 12-box model, the calculated mole fractions in 1989 are lower than the Simpson et al. [2004] values by 30%. The C$_2$Cl$_4$ measurements by Koppmann et al. [1993] in 0–30°S in August/September 1989 are approximately the same as the box model estimates for that time but their observations are substantially lower than our estimates for 0–30°N. The AGAGE measurements at Cape Grim projected back to 1995–1997 are approximately 10% lower than those reported for Cape Grim samples by Butler et al. [1998] and Elkins et al. [2001]. This is also true for the Mace Head measurements projected backward compared with their measurements at Barrow, Alaska. NOAA measurements through 2004 are shown by Thompson et al. [2004]. They confirm that, as seen in the AGAGE measurements, the C$_2$Cl$_4$ values in 2001–2003 are 10–15% less than the values in 2000. The AGAGE measurements at Mace Head are approximately 25% larger than the Dimmer et al. [2001] measurements in the Arctic in August/September, 1997 and in the North Atlantic in April/May, 1998 if the McCulloch et al. [1999] emissions are used. The currently observed AGAGE C$_2$Cl$_4$ mixing ratios are lower than those reported by Wiedmann et al. [1994] for 1982–1989 (McCulloch et al. [1999] do not provide emission estimates before 1988) and Blake et al. [1996a].

C$_2$HCl$_3$ (and C$_2$Cl$_4$) both show substantial fluctuations in their annually averaged growth rates with small, but uncertain, downward trends due to the relatively short period of observations. The very short tropospheric lifetime of C$_2$HCl$_3$ results in large spatial and seasonal variability which makes comparisons with earlier measurements problematic, although the AGAGE measurements are within the range reported by Ko and Poulet [2003]. For all three chlorinated solvents there are some discrepancies which suggest significant unresolved differences in the absolute calibration scales used by the various measurement groups.

5. Seasonal Cycles

The average seasonal cycles at both Mace Head (shown in Figure 4) and Cape Grim (shown in Figure 5) are very regular and narrowly defined for these chlorinated solvents (see also Table 1). These average annual seasonal cycles have been computed directly from the baseline data for each site. They are calculated by removing the long-term trend fit, (essentially the same as the combination of the a, b and d terms in the empirical model fit given by equation (1)), from the data and then averaging this residual for each of the months/years to produce the overall averaged seasonal cycle,
using the techniques outlined by Thoning et al. [1989]. The phase of the annual cycles varies by less than 2 months between the species at each site, with minima in the respective mid/late summers, and maxima in late winter/early spring. At Mace Head, baseline mole fractions of C₂HCl₃ show a seasonal cycle with highest monthly mean mole fractions in winter (January–February) and the lowest values in the middle of summer (June–August). This seasonal cycle is earlier in the year compared with C₂Cl₄ which has its maximum in early spring (March–April) and minimum in late summer (August–September), while the cycle of CH₂Cl₂ is later than both with its peak in early spring (April) and lowest values in late summer (August–September). At Cape Grim the situation is similar with maxima occurring in late winter (August–September) and minima in late summer (February), with the phase of C₂Cl₄ being a few weeks earlier than that of CH₂Cl₂.

[30] At Mace Head the observed amplitude (peak minus mean) of the seasonal cycle of CH₂Cl₂ is about 18% of the mean, for C₂Cl₄ about 40% of the mean and for C₂HCl₃ about 120% of the mean. In the order CH₃Cl₂, C₂Cl₄ and C₂HCl₃, these species show increasing atmospheric reactivity with respect to oxidation by tropospheric OH consistent with their decreasing atmospheric lifetimes CH₂Cl₂-140 days, C₂Cl₄-100 days, and C₂HCl₃-5 days [Montzka and Fraser, 2003].

[31] There is a marked shift in the phase of the seasonal cycle, with the maximum and minimum months coming earlier in the year with increasing atmospheric reactivity [see also Goldstein et al., 1995]. Similar differences in phase and intensity of the seasonal cycles have been reported previously in observations of nonmethane hydrocarbons made from aircraft over the North Atlantic Ocean [Penkett et al., 1993]. Similarly, at Cape Grim C₂Cl₄ and CH₂Cl₂ have winter maxima (late August, early September, respectively) and the minima for both species are in February. These phases at Cape Grim are similar to those for the HCFCs reported by O’Doherty et al. [2004] and for CH₄ [Cunnold et al., 2002].

6. Estimating Emissions From Europe

6.1 Using a Back-Attribution Technique

[32] The NAME Lagrangian dispersion model [Ryall et al., 2001], driven by 3D synoptic meteorology from a numerical weather prediction model (UK Meteorological Office), has been used to determine the fraction of air arriving at Mace Head (in a grid volume 0.833° × 0.555° × 0–200 m centered on Mace Head) from different European regions at 1-hour intervals over the 10-year period, 1995–2004. The NAME model assumes that each gas behaves as an inert tracer and no corrections are made for chemical depletion en route to Mace Head. Baseline points are selected by excluding observations recorded when the air at Mace Head has contributions from east of the station or from southerly latitudes or when the air is not well mixed (defined as when the contribution to the Mace Head air concentration has a significant local component). Outlying concentrations de-
fined as baseline by air origin are removed before fitting a quadratic function to a rolling 3-month window of baseline points and then mean-smoothing within a rolling 4-week period. This procedure is somewhat different from that used to define the AGAGE baseline mole fractions. The AGAGE procedure uses a rolling 4-month window and it does not use mean-smoothing. The largest difference is that the AGAGE procedure uses a statistical method to remove pollution events and as a result does not filter out nonpollution events from southerly latitudes. Previously we have shown that the difference between the two baseline selection procedures for other gases is small [O’Doherty et al., 2001]. Here, the monthly mean differences for CH$_2$CL$_2$ and C$_2$Cl$_4$ average approximately 1% (with a standard deviation of 3%). These differences are comparable to the uncertainties in the mean values given in Table 1. However, it is noteworthy that the amplitude of the CH$_2$Cl$_2$ seasonal cycle at Mace Head in 1996 is 5.4 ppt (∼14%) higher using the NAME model baseline values, where the southerly transport events have been eliminated from the monthly mean calculations. By subtracting the time-varying baseline concentrations from the total measurements a time series of excursions from the baseline values of each observed trace gas is generated for the period 1995–2004 inclusive. The observed deviations from baseline are averaged over each 1-hour period with all negative values considered to be zero. These perturbations are driven by emissions on regional scales that have yet to be fully mixed on the hemisphere scale. This time series, together with the NAME model estimates of where the air originated from and the relative contribution from each area for each observation, are used to estimate the emission distribution of each gas over western Europe. The iterative best fit technique, simulated annealing, is used to derive these values on the basis of a statistical score (cost function) combining correlation coefficient, normalized mean square error and fraction within a factor of two [Manning et al., 2003]. The technique, starting from a set of random emission maps, searches for the emission map that leads to a time series at Mace Head that most accurately mimics the observations. The NAME model has not attempted to model OH induced loss during transport.

This method has previously been applied to CFC-11, CFC-12, methane and nitrous oxide [Manning et al., 2003], HFCs [O’Doherty et al., 2004], methyl bromide [Simmonds et al., 2004] and methyl chloroform [Reimann et al., 2005]. The technique assumes that the air arriving at the edge of the domain is baseline, an assumption that does not strictly hold especially when the air mass origin is eastern Europe or the Mediterranean. The model accuracy improves as the distance to Mace Head is reduced and the number and magnitude of transport events increases. The model results have their greatest uncertainty in the southeast area of the European domain from where transport to Mace Head is infrequent and complicated by complex flow around the Alps. In order for the best fit algorithm to provide robust solutions for every area within the domain each region needs to significantly contribute to the air concentration at Mace Head. If the signal from an area is only rarely or weakly seen at Mace Head then its impact on the cost function is minimal and the inversion method has little skill at determining its true emission. In order to meet this criterion over the European domain using Mace Head data, it was necessary to group the solutions into 2-year periods as well as combine distant regions into large areas. For this reason the Mediterranean and southern Italian area have been excluded from the analysis, although emissions from these areas will influence the solution by increasing the emissions at the southeast edge of the domain.

There is no absolute method of defining the errors associated with these best fit estimates; the errors are compounded from errors in the meteorology, from the numerical weather prediction model, in the transport parameterizations in NAME and in the observations. The inversion technique also introduces errors as it assumes that all of the emissions are constant in time and are geographically static within the study period and that all areas of the domain have sufficient transport to Mace Head. Above (below) baseline air entering the domain will lead to elevated (depressed) emission estimates at the edge of the domain. Emissions local to Mace Head will have a proportionally higher impact on the observed signal than more distant sources and may, if they are large, make distant emissions difficult to detect. To quantify the robustness of the solutions the inversion method is applied to each trace gas for each 2-year period 8 times and the range of solutions are indicated in the table captions. Each time a solution is required, each observation data point is perturbed by a random noise factor. The noise factor has a mean of zero and a standard deviation equal to the noise in the baseline values, namely the standard deviation of the observations classed as baseline.

The estimated UK emissions from the NAME model are given in Table 3 and European emissions derived from the NAME model and from industry data [McCulloch et al., 1999, updated in 2004] are shown in Table 4. The geographical area covered by the NAME estimates and the industry estimates are not identical. The industry estimates are based on EU-15 activity data as a whole. (15 EU counties, United Kingdom, Ireland, France, Germany, Denmark, Netherlands, Belgium, Luxembourg, Spain, Portugal, Sweden, Italy, Austria, Greece, and Finland). The NAME estimates are presented on a defined grid covering northwest and central Europe. Emissions outside this modeled domain will possibly be included in the maps as edge effects, i.e., the grids at the edge of the domain may be

<table>
<thead>
<tr>
<th>Solvent</th>
<th>95–96</th>
<th>96–97</th>
<th>97–98</th>
<th>98–99</th>
<th>99–00</th>
<th>00–01</th>
<th>01–02</th>
<th>02–03</th>
<th>03–04</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>11.1</td>
<td>12.7</td>
<td>11.4</td>
<td>8.6</td>
<td>11.5</td>
<td>10.1</td>
<td>9.1</td>
<td>9.7</td>
<td>8.4</td>
</tr>
<tr>
<td>C$_2$HCl$_3$</td>
<td>7.0</td>
<td>6.9</td>
<td>7.2</td>
<td>6.5</td>
<td>6.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$Cl$_4$</td>
<td>3.5</td>
<td>3.4</td>
<td>3.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
elevated, however a source outside the domain would have to be very significant (e.g., >10 kt yr\(^{-1}\) in central Italy or greater for more distant areas) to be systematically observed at Mace Head. Also the number of events from these very distant sources arriving at Mace Head will be very limited and make any emission estimates from these areas very uncertain.

6.2. Using Two CO Ratio Methods

[36] For comparison, also included in Table 4 are estimates of regional emissions determined from molar ratio calculations using CO emission inventories [see, e.g., Reimann et al., 2005]. This method assumes that the sources of the halocarbons and CO are colocated. While not strictly correct, it is reasonable to assume that both the halocarbons and CO are emitted from many diffuse, spatially similar anthropogenic sources.

[37] The emissions are estimated from the pollution events identified by the AGAGE pollution algorithm. The occurrence of CO pollution events is assumed to indicate the presence of air from the European continent and/or from the UK. Indeed the proportion of CO pollution events annually is similar to the proportion of back trajectories at Mace Head which come from the wind sector defined by the European continent. Annual emissions are estimated by summing the (CO – baseline) mole fractions in all the CO pollution events for the year and then also summing the (mole fractions – baseline values) for the solvents in the same CO pollution events. Recognizing that CO and solvent sources are not always collocated, the relatively few values of CO and the solvents in identified solvent pollution events in which CO pollution has not been identified are also included in the respective sums. The sums are converted from ppb by volume to ppb by mass by multiplying by the respective molecular weights and the solvent emission estimates for the EU-15 region are obtained by dividing the annual sum for an individual solvent by the annual sum for CO and multiplying by the reported CO annual emissions for the EU-15 region [Vestreng et al., 2004].

<table>
<thead>
<tr>
<th>Year</th>
<th>NAME Model</th>
<th>CO NAME Inventory</th>
<th>CO Inventory</th>
<th>Industry</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>CH(_2)Cl(_2) kt/yr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>95/96</td>
<td>(66)</td>
<td>(65)</td>
<td>(62)</td>
<td>147</td>
</tr>
<tr>
<td>96/97</td>
<td>88</td>
<td>71</td>
<td>79.5</td>
<td>152</td>
</tr>
<tr>
<td>97/98</td>
<td>106</td>
<td>90</td>
<td>93.5</td>
<td>156</td>
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<td>98/99</td>
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<td>53</td>
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<td>75.5</td>
<td>151</td>
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<td>54</td>
<td>142</td>
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<td>02/03</td>
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<td>139</td>
</tr>
<tr>
<td>03/04</td>
<td>54</td>
<td>61</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>C(_2)HCl(_3) kt/yr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>95/96</td>
<td>(43)</td>
<td>(39)</td>
<td>(56.5)</td>
<td>77</td>
</tr>
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<td>52</td>
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<td>39</td>
</tr>
<tr>
<td>99/00</td>
<td>40</td>
<td>32</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>C(_2)Cl(_4) kt/yr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>95/96</td>
<td>(40.5)</td>
<td>(40.5)</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>96/97</td>
<td>45</td>
<td>26</td>
<td>26.3</td>
<td>60</td>
</tr>
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<td>97/98</td>
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<td>56</td>
</tr>
<tr>
<td>98/99</td>
<td>33</td>
<td>30</td>
<td>24.3</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*NAME-derived European emission estimates (2-year averages) in kt (Gg) per year (range of solutions fall within ±16, ±9 and ±2 kt/yr respectively). Industry estimates (updated by A. McCulloch in 2004) are based on industry sales data. CO inventory estimates are derived from molar ratio calculations using CO emission inventories [Reimann et al., 2005]. Numbers in parentheses are the averages of less than 6 months of measurements in year 1 plus 12 months of measurements in year 2.
2.8. The NAME European emission estimates for CH2Cl2 increase from 1995 up to 1998 and then show a decline, which is consistent with the NAME CO inventory and the CO ratio method used by Reimann et al. [2005]. This compares with industry estimates which show a small increase up to 1999/2000 and then a decline. In Figure 6a are plotted the European emissions estimated by the NAME inversion and the NAME CO ratio method compared with industry estimates of CH2Cl2 emissions. As expected the NAME model and CO inventory methods closely follow the decline in CH2Cl2 pollution events, while the industry estimates of emissions are much more constant over time. Figure 6b maps the NAME model estimates of the regional CH2Cl2 emissions. Figures 7a, 7b, 8a, and 8b show comparable plots for C2HCl3 and C2Cl4, respectively. C2HCl3 and C2Cl4 both show an overall reduction in the level of European emissions; however, the NAME model estimates indicate much greater interannual variability in the emissions of C2HCl3.

[40] All three methods of estimating emissions have large uncertainties, although in previous comparisons of the NAME and industry estimates of other gases, agreement has been within a factor of two or less. In this study, all three emission estimates for C2HCl3 agree within a factor of two. Similarly, NAME and industry estimates for C2Cl4 are also within a factor of two, with estimates derived from the molar ratio to CO slightly lower than the NAME estimates, but more than a factor of two lower than the industry estimates. Although, industry-derived emission estimates for CH2Cl2 are also within a factor of two during 1996–1998, they are considerably higher from 1999 to 2004, than either the NAME or CO correlated estimates, which are in much closer agreement. The relatively close agreement for CH2Cl2 calculated by the three methods, compared with the larger disagreement for CH2Cl2 is surprising. As noted above, the NAME model has the greatest uncertainty for emissions from more distant regions, such as the Mediterranean and eastern Europe. With the longer travel distance to Mace Head from these regions and the high reactivity of C2HCl3 with OH, some depletion during transport would be expected to occur. Trichloroethene depletion during summertime was estimated to be a factor of between 2 and 10 compared to other more chemically inert trace gases depending on the travel time to Mace Head [Derwent et al., 1999]. Without a clearer understanding of possible seasonality in the emissions of C2HCl3, it is difficult to quantify losses during transport. During the winter months removal by OH should be minimal and the relative mole fractions of these halocarbon solvents in regionally polluted air masses should more accurately represent their relative emissions. The regression slope of all Mace Head observations, identified as pollution, for C2Cl4 vs. CH2Cl2 (r2 > 0.8) on a mass basis was calculated to be 0.85 ± 0.04, which is greater than the relative emission ratio of 0.47 (by mass) reported for the UK National Atmospheric Emissions Inventory [Passant, 2004], and also greater than the industry-derived European emission estimates average ratio of C2Cl4 vs. CH2Cl2 of 0.45. However, the same average ratio calculated using the NAME model European emission estimates are approximately 0.74 (average 2001–2002); 0.66 (average 2002–2003); and 0.61 (average 2003–2004). If just the wintertime NAME emissions are used the ratio drops to 0.45, in closer agreement to the other industry-derived emission ratios.

[41] There are a number of possible explanations for the disagreement between the European emission estimates for CH2Cl2 by the NAME model and industry. As noted in
section 6, the geographical areas covered by the NAME and industry estimates are not the same; however, the majority of the major emitting countries are covered by both methods. The UB98 calibration scale for CH$_2$Cl$_2$ is based on a single Linde primary calibration mixture. Recent comparisons of calibrated AGAGE CH$_2$Cl$_2$ in situ measurements with NOAA flask data at Mace Head show an absolute calibration difference of 8.8 ± 4%, with NOAA data higher (P. B. Krummel, CSIRO, comparisons include a NOAA scale change in 2003). If the AGAGE measurements were reported in the NOAA scale this would improve agreement to within a factor of 2 in most years. However, industry estimated CH$_2$Cl$_2$ emissions would still be a factor of 2.1–2.6 greater than NAME derived emissions estimates during 1999–2003.

[42] Emissions from Europe may be overstated by the industry estimates in a number of ways despite the fact that global emissions from the same database are consistent with our 12-box model results, as well as those reported by Trudinger et al. [2004]. Emissions are derived from consumption data and are assumed to occur in the same geographical area as the consumption (sales). Material shipped directly by producers is assumed as consumption at the destination, but significant exports from Europe of the solvents (by chemical merchants, not producers) or in equipment containing the solvents would result in the true

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**Figure 6a.** Estimates of European emissions (k tonnes yr$^{-1}$) of CH$_2$Cl$_2$ from the NAME model inversion and CO ratio methods.

**Figure 6b.** NAME-derived European emission map for CH$_2$Cl$_2$, 1995–1996 and 2003–2004.
emissions in Europe being lower than derived from consumption data.

[43] Material that is emitted and becomes dissolved in surface water might be transported over a significant distance before temperature changes might cause it to be reemitted to the atmosphere [Moore, 2004]. Notably, of the three solvents CH$_2$Cl$_2$ has the highest water solubility (13.2g/liter @20°C [U.S. Environmental Protection Agency, 1994]).

[44] There may be a significant seasonal variability in the emissions of each individual halocarbon. For example, apparent wintertime emissions of CH$_2$Cl$_2$ at Mace Head are generally higher than apparent summertime emissions, although in some years, notably in 1999, 2000 and 2002 this is not the case.

[45] One other major area of uncertainty in attempting to reconcile the different emission estimates lies in quantifying the relative loss rates of each individual solvent during transport through the atmosphere. At the extremes of the NAME model domain OH removal will be amplified by larger OH concentrations, and higher temperatures during the summer months, leading to much shorter tropospheric lifetimes than the annual average lifetimes.

[46] There may also be unaccounted for sinks, such as hydrolysis, dry deposition and biodegradation which could perturb the relative emission ratios from the primary source regions. Mabey and Mill [1978] estimated a half-life of 704 years for the hydrolysis of CH$_2$Cl$_2$ in water. However, biodegradation in aqueous media by aerobic and anaerobic bacteria common in soil and sludge appears to...
be a more rapid process on the order of hours or weeks [Stover and Kincannon, 1983; Davis and Madsen, 1991]. No single factor appears to account for the inconsistencies between industry-derived, NAME model-derived and CO inventory estimated emissions. In order to resolve some of these questions, high-frequency measurements from additional sites in Europe are required.

7. Emissions of CH$_2$Cl$_2$ From Biomass Burning

[47] On the basis of CH$_2$Cl$_2$/CO molar emission ratios (2.5 ± 0.6 × 10$^{-5}$) measured in African savanna fires [Rudolph et al., 1995], a globally significant annual biomass burning CH$_2$Cl$_2$ source of 49 Gg Cl has been reported [Lobert et al., 1999]. Scheeren et al. [2002] reported a larger, but more uncertain, molar CH$_2$Cl$_2$/CO emission ratio (4.4 ± 4.7 × 10$^{-5}$) for Indian/SE Asian fires, largely involving biofuels (dung) and agricultural waste.

[48] Large smoke plumes from wildfires occasionally pass over Cape Grim, Tasmania. During these events, elevated levels of CO, CH$_3$Cl and CH$_3$Br (and other trace gases) are observed. During 2003, Cape Grim sampled fire plumes during January–March and November, in particular from Flinders Island (300 km ENE, area burnt 160 km$^2$, 10–12 January), Robbins Island (20 km E, 35 km$^2$)

Figure 8a. Estimates of European emissions (k tonnes yr$^{-1}$) of C$_2$Cl$_4$ from the NAME model inversion and CO ratio methods.

Figure 8b. NAME-derived European emission map for C$_2$Cl$_4$, 2001–2002 and 2003–2004.
17 November) and the Tasmanian west coast (50 km SSE, 400–500 km², 21–23 November) (Figure 9). These fire plume events at Cape Grim are useful to define the chemical characteristics of wildfires, as trajectory analyses and the lack of urban tracers (for example HFC-134a) show that these fire plumes are not contaminated by urban emissions, which would typically include CH₂Cl₂. The pollution events of 25 January 2003 (Figure 10) are typical of urban (Melbourne) pollution events observed at Cape Grim. The trace gas variability of CO, HFC-134a, CH₂Cl₂ and CH₃Cl observed at Cape Grim during January and November 2003 are shown in Figures 10a and 10b, respectively. From these data, CH₃Cl/CO molar emission ratios of (0.2–1.3) × 10⁻³ can be derived. These are similar to ratios reported for savanna grassland, tropical and extratropical forests, biofuels and agricultural waste ((0.03–1.7) × 10⁻³) [Blake et al., 1996b; Andreae and Merlet, 2001; Scheeren et al., 2002]. In contrast, the CH₂Cl₂/CO molar emission ratios observed in the 2003 Tasmanian fires are (<1–6) × 10⁻⁷, approximately two orders of magnitude lower than the CH₃Cl/CO ratios previously reported [Rudolph et al., 1995; Scheeren et al., 2002].

Africa accounts for about 50% of the global area burnt each year. However, Australian biomass burning is significant on a global scale, with 16% (600,000 km²) of the global area and 8% (265 Tg) of the global dry matter burnt in 2000 [Ito and Penner, 2004; Tansey et al., 2004]. More studies are required to define representative molar ratios for Australian wildfires, but the Tasmanian fires studied thus far are an insignificant source of CH₂Cl₂. These data suggest that further field studies are required to assess whether biomass burning is a significant global source of CH₂Cl₂.

8. Conclusions

Continuous measurements of CH₂Cl₂, C₂HCl₃, and C₂Cl₄ at Mace Head, Ireland (1995–2004) and at Cape Grim, Tasmania (1998–2004) have been made (every 4 hours) using automated GC-MS instruments. These measurements indicate that the atmospheric mole fraction of CH₂Cl₂ has been decreasing at Mace Head from 1995 to 2004 at a mean rate of 0.7 ± 0.1 ppt yr⁻¹, although over the shorter timeframe from 1998 to 2004 this decrease has been only about 0.3 ± 0.1 ppt yr⁻¹. Over the same time frame there has been a small positive trend (0.05 ± 0.01 ppt yr⁻¹) in CH₂Cl₂ at Cape Grim. In comparing our observations with other earlier measurements of the three chlorinated solvents there is a difficulty in that different measurements often are not consistent in space and time and many measurements were.

Figure 9. Location of three wildfires that impacted on atmospheric composition at Cape Grim, Tasmania, during 2003 (wildfire 1: Robbins Island, 20 km E of Cape Grim, burnt area 35 km², 17 November; wildfire 2: Flinders Island, 300 km ENE, 160 km², 10–12 January; and wildfire 3: Tasmanian west coast, 50 km SSE, 400–500 km², 21–23 November).
Simpson et al. calculated with the Thompson et al. from 1999 to 2003. The change in emission/C0 are much higher than those
> C H McCulloch et al. mixing ratios in 2002 reported by in
in 2000 and 260 ± 1100 Gg yr (lifetime (two sigma)
there is an approximately 330 ± 20 Gg yr
[1999]. These estimates and those of the NOAA site at Barrow, Alaska, Butler
being a measure of the maxima in the seasonal cycles of CH
in 2000 and 205 Gg yr
/emissions decreasing by about 50% and C
and CO observations at Cape Grim, Tasmanian during (a) January
, 2004] show an
approximately 15–20% decrease in CH
amplitudes in the order C
/Cl
/Cl4
CNH monitoring sites [Thompson et al., 2004] show an
global lower-tropospheric average for C
2 Cl4 in 2002 of 2.6 ppt that is about 25% lower than the UCI reported value of 3.5 ppt [Simpson et al., 2004]. The short tropospheric
time of C2 HCl3 results in large spatial and seasonal variability which makes comparisons with earlier measurements problematic, although the AGAGE measurements are within the range reported by Ko and Poulet [2003].

All three solvents have strong annual cycles with amplitudes in the order C2 HCl3 > C2 Cl4 > CH2 Cl2, as expected from their respective atmospheric lifetimes largely determined by reaction with OH. The maxima and minima in the phases of the annual cycles at Mace Head occur earlier in the year with decreasing atmospheric lifetime, with C2 HCl3 (lifetime ~5 days) peaking in January–February, with the lowest monthly mean mole fractions in June–July. This contrasts with the other two chlorinated solvents, C2 Cl4, and CH2 Cl2, with maxima in March–April, and minima in August–September (lifetimes ~100, and 140 days, respectively). At Cape Grim the maxima in the seasonal cycles of CH2 Cl2 and C2 Cl4 occur in late winter (August–September) and minima in late summer (February), with the phase of C2 Cl4 being a few weeks earlier than that of CH2 Cl2 consistent with its shorter atmospheric lifetime.

Annual emission estimates of CH2 Cl2 from 1995 to 1997 calculated in the 12-box model are in the range 626 ± 11 Gg yr−1 compared with emission estimates of 515 ± 22 Gg yr−1 from 1999 to 2003. The change in emission estimates between the two periods is statistically significant. Industry emission estimates of CH2 Cl2 in 1995 to 1997 [McCulloch et al., 1999] are consistent with the anthropogenic contribution to the global emission estimates provided that 15 ± 15% of the emissions are nonanthropogenic.

The estimated emissions of C2 Cl4 calculated with the 12-box model are 250 Gg yr−1 in 2000 and 205 Gg yr−1 in 2002. The average annual emission over the period 1999 to 2003 is 228 Gg yr−1, compared with the industrially derived global emission estimates of 268 ± 27 Gg yr−1 (two sigma) for 1999 and 2000, McCulloch et al. [1999]. These estimates may also be compared with reported annual emissions of C2 Cl4 of 330 ± 20 Gg yr−1 in 2000 and 260 ± 15 Gg yr−1 in 2002 reported by Simpson et al. [2004].

European emission estimates of CH2 Cl2 from atmospheric observations and industry sales data show an overall decline during 1995–2004 with a significant peak (20%) in model emissions in 1997–1999, compared to 1995–2004; only a small corresponding increase (5%) was found in industry emission data over this same period. Industry estimates of European emissions of C2 HCl3, and C2 Cl4 both show significant declines from 1995 to 2003, with C2 HCl3 emissions decreasing by about 50% and C2 Cl4 emissions by about 30%. European emissions of C2 HCl3 estimated from industry sales data are within a factor of two of those estimated using the NAME model and the two CO emission inventories. For C2 Cl4 there is an approximately factor of two difference between the industry and pollution event derived estimates. However, industry derived European emissions of CH2 Cl2 are much higher than those estimated by the other two methods. At present, we are unable to reconcile these differences, but believe that a

Figure 10. HFC-134a, CH2 Cl, CH2 Cl2 and CO observations at Cape Grim, Tasmanian during (a) January and (b) November 2003. The trace gas enhancements during the three fire episodes (locations shown in Figure 9) are shaded.
number of different factors are involved. These include the potential underestimation of emissions from the more remote regions of Europe by the NAME model, exports of solvents outside of Europe not reflected in the method of calculating emissions from industry data, and a possible error in absolute calibration. Additional observations at other European sites are needed to improve our estimates of European emissions and a study is currently in progress from measurements of CH$_3$Cl at the two SOGE monitoring sites at the Jungfraujoch, Switzerland, and Monte Cimone, Italy (S. Reimann and M. Maione, personal communication, 2005).

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Zischle, A. J., A. J. Manning, Climate Research, Met Office, Exeter EX1 3PB, UK.