Global trends and emission estimates of CCl$_4$ from in situ background observations from July 1978 to June 1996


Abstract. Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment/Advanced Global Atmospheric Gases Experiment (ALE/GAGE/AGAGE) measurements of CCl$_4$ at five remote surface locations from 1978 to 1996 are reported. The Scripps Institution of Oceanography (SIO) 1993 absolute calibration scale is used, reducing the concentrations by a factor of 0.77 compared to previous ALE/GAGE reports. Atmospheric concentrations of CCl$_4$ reached a peak in 1989–1990 of 104.4 ± 3.1 parts per trillion (ppt) and have since been decreasing 0.7 ± 0.1 ppt yr$^{-1}$. Assuming an atmospheric lifetime of 42 ± 12 years, the emissions averaged 94±22 x 10$^6$ kg from 1979 to 1988 and 49±12 x 10$^6$ kg from 1991 to 1995. The reduction in the emissions in 1989–1990 coincided with a substantial decrease in the global production of the chlorofluorocarbons (CFCs). The total emission of CCl$_4$ from countries that report annual production is estimated to have declined from 11% in 1972 to 4% in 1995 of the CCl$_4$ needed to produce the CFC with a substantial decrease in the global production of the chlorofluorocarbons (CFCs). This use increased rapidly from the mid-1950s to the 1980s, with the manufacture of CFC-12 (CCl$_2$F$_2$) and CFC-11 (CCl$_3$F). Since the introduction of the Montreal Protocol [World Meteorological Organization (WMO), 1988] and its various amendments, which listed CCl$_4$ as a controlled substance, large-scale production has declined rapidly. This decline has accelerated with the global phaseout of CCl$_2$F$_2$ and CCl$_3$F production, which consumed 80–90% of the total CCl$_4$ production.

Tropospheric mixing ratios of CCl$_4$ increased steadily from the mid-1970s to 1990, and the results from both in situ and flask measurements have been summarized in recent reports [Fraser et al., 1994; Sunhuesa et al., 1995]. Rates of accumulation were reported as 1.6 parts per trillion (ppt) yr$^{-1}$ (1.3 ± 0.1% from 1978 to 1985 [Simmonds et al., 1988] (henceforth referenced as S88), 1.2 ± 0.2 ppt yr$^{-1}$ from 1979 to 1990

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Paper number 98JD01022.
0148-0227/98/98JD-01022$^5$0.00

16,017
lifetime of CCl₄ can be obtained from global measurements by inverse methods when sufficiently accurate estimates of industrial emissions are available. Unfortunately, this information has been lacking for CCl₄, and these estimates have had to be derived indirectly from the more accurately known production and estimated emissions of the chlorofluorocarbons and the stoichiometry for the conversion of CCl₄ to these compounds [Simmonds et al., 1983; S88]. Conversely, it is possible to use the lifetime of CCl₄ calculated from realistic theoretical models [Golombek and Prinn, 1986; Ko and Jackman, 1994], coupled with the long-term global measurements, to derive global emissions. In this paper we use 18 years of CCl₄ measurements obtained from 1978 to 1996 at five ALE/GAGE/AGAGE stations to estimate global trends, which are then used to calculate global emissions. We have also compared the recent decline in the atmospheric mixing ratios of CCl₄ observed at our measurement sites to the global emissions of CFCs, for which production is more accurately known, to determine whether the decline in the atmospheric abundance of CCl₄ is consistent with decreases in CFC production.

2. Measurements and Calibration

2.1. Experimental

CCl₄ measurements were obtained at Ragged Point, Barbados (13°N, 59°W), and Cape Grim, Tasmania (41°S, 145°E), over the period July 1978 to June 1996. The data set also includes measurements at Cape Meares, Oregon (45°N, 124°W), for the period December 1979 to June 1989; Cape Matatula, American Samoa (14°S, 171°W), from December 1979 to June 1989 and again from January 1992 to June 1996; Adrigole, Ireland (52°N, 10°W), from July 1978 to December 1983; and Mace Head, Ireland (53°N, 10°W), from February 1987 to June 1996. All stations use identical microprocessor-controlled gas chromatographs with packed methyl silicone columns, and electron capture detectors determine CCl₄ in near real time with a 5-mL sample volume [Prinn et al., 1983, 1987, 1992]; calibration involves an alternate analysis of ambient air and air from an on-site secondary standard. Typical precisions for CCl₄ based on repeated measurements of the calibration standards at the different stations are ~0.5%.

2.2. Calibration

GAGE working standards were prepared and assigned concentrations prior to 1990 by R. Rasmussen (Oregon Graduate Institute (OGI)). From 1990 on, this task was performed by P. Fraser at Commonwealth Scientific and Industrial Research Organisation (CSIRO), and concentrations were assigned to the working standards based on calibration against three working standards prepared by R. Rasmussen. Therefore all ALE and GAGE measurements were previously assigned concentrations based on the so-called OGI 1980 scale. Various intercalibration exercises with other independent laboratories produced a 25% range in the CCl₄ measurements, and the average CCl₄ values from five non-GAGE laboratories were ~25% lower than those from GAGE. These five laboratories also agreed to within 10% for CCl₄ [Fraser et al., 1994].

CCl₄ concentrations are reported here as dry air mole fractions in ppt (parts in 10⁻¹²) on the Scripps Institution of Oceanography (SIO) 1993 absolute scale developed under the AGAGE project. The SIO "bootstrap" calibration method combines the absolute calibration for CO₂ [Keeling et al., 1976] with separate determinations of the ratios of N₂O to CO₂ [Weiss et al., 1981] and of halocarbons to N₂O [Bullister and Weiss, 1988]. The application of the method to obtain the AGAGE 1993 calibrations of the halocarbons CCl₃F and CCl₃Br has been summarized by Cunnold et al. [1994]. For CCl₄ the relative standard deviation of the seven independent primary standards which together constitute the SIO 1993 scale for this compound, as determined by gas chromatographic intercomparison, is 0.6%. We estimate that the total systematic uncertainty of the SIO 1993 scale for CCl₄ is ~3%.

The AGA CCl₄ measurements have been converted to the SIO 1993 scale based on eighteen 35-L working standards of Cape Grim background air that have been measured against SIO 1993 primary standards at SIO and against OGI GAGE standards at Cape Grim. The results of these comparisons are that the AGA/GAGE measurements by Simmonds et al. [1983, 1988] must be multiplied by 0.770 to place them on the SIO 1993 scale. (This is equivalent to saying that the SIO 1993 scale for CCl₄ possesses a factor ε = 0.6233, relative to the original working standards used in ALE.) Although the standard error (standard deviation divided by √n) of the SIO measurements is ~0.1%, the standard deviation of the measured ratios is ~0.5%. This difference is due to the larger imprecision of the HP5880A (GAGE) measurements at Cape Grim compared with those obtained in the laboratory at SIO. Repeated measurements of the air in four tanks, ~20 times per year from 1990 to 1995 at Cape Grim, where values were assigned to all the GAGE calibration gases during this period, indicate that system calibration in the field is being maintained for CCl₄ with an accuracy in any 1 year of better than 1% (1σ) and with an accuracy over the 6-year period of better than 0.1 ppt yr⁻¹.

The continuity of the calibration scale prior to 1990 was originally in question for CCl₃F and CCl₃Br [Cunnold et al., 1994]. Similar questions exist for CCl₄. Comparisons similar to those described by Cunnold et al. [1994] have reassured us that any calibration changes were small (<2%). Figure 1, for example, shows a polynomial fit to the concentrations in the same air samples in our 35-L tanks measured at different times and ratioed to the first measurements of the concentrations. It
suggests that the calibration scale drifted upward by \(-2\%\) over the 1984–1986 period. It should be noted, however, that we no longer have access to all the OGI calibration records, and the measurement dates used to make Figure 1 are only accurate to \(\pm 6\) months after 1984. Figure 2 shows comparisons between the Cape Grim ALE/GAGE time series of measurements and the \(\text{CCL}_4\) concentrations in archived air samples collected at Cape Grim in 35-L tanks under “baseline” conditions [Fraser et al., 1991; Cunnold et al., 1994; Langenfelds et al., 1996]. These air samples, which contain air that was collected as far back as April 1978, were analyzed over the past several years on the HP5880A (GAGE) gas chromatograph at Cape Grim. The ratio of the values is shown in Figure 2. It is immediately obvious that \(\text{CCL}_4\) is very stable in the 35-L tanks. However, prior to mid-1984 the mean archive air–GAGE \(\text{CCL}_4\) ratio is \(0.984 \pm 0.004\). From mid-1988 on, the mean ratio is \(1.005 \pm 0.003\). Therefore, from the combination of the archived air comparisons (Figure 2) and the repeated measurements on the standards (Figure 1), we conclude that an upward shift in the \(\text{CCL}_4\) calibration of 1.5–2.0% probably occurred between 1984 and 1988 (with some evidence that it occurred between 1984 and 1986). Because of the small size of the shift and the uncertainty about its timing, no adjustment has been made to the AGA time series. However, its effect on the results is illustrated, and it is included in the assessment of error bars.

The nonlinearity in response to \(\text{CCL}_4\) concentration variations has been evaluated for one GAGE HP5880 instrument using sample dilutions ranging over a factor of more than 3. The nonlinearity is weak and amounts to \(-2.5\%\) for a concentration change of a factor of 3. Over the period 1978–1996, atmospheric \(\text{CCL}_4\) concentrations have changed by \(-20\%\). Therefore the absence of a correction for nonlinearity in the GAGE observations might have contributed an error of \(-0.5\%\) to the measured change in concentration over the entire period if this instrument is typical. This uncertainty is significantly less than that described in the previous paragraph and is considered to be negligible. Moreover, measurements with the AGAGE HP5890s, which possess similar nonlinearities in response, are being automatically corrected.

3. Analysis of the Measurements

The monthly mean dry air mole fractions \(\chi\) expressed as parts in \(10^{12}\) and the standard deviations \(\sigma\) computed from up to 120 (ALE), 360 (GAGE), and 1080 (AGAGE) measurements made each month are illustrated in Plate 1. The data are available from the Carbon Dioxide Information Analysis Center (CDIAC) at the U.S. Department of Energy (Oak Ridge National Laboratory, Tennessee; through internet at cdp@ornl.gov). These global measurements show that the atmospheric burden of \(\text{CCL}_4\) has decreased since about mid-1990, in accordance both with its restricted use under the Montreal Protocol and with the decline in its use as a feedstock for the production of CFCs. The observed mole fractions \(\chi\) at each site have been fitted with an empirical model and expressed as functions of time \(t\) (in years), represented by

\[
\chi(t) = a_0 + b_0(t - N) + \frac{d_0}{3N^2} \left( \frac{3(t - N)^2}{N^2} - 1 \right) \\
+ c, \cos 2\pi t + s, \sin 2\pi t
\]  

(1)

where \(t\) is measured in years from July 1, 1978, the start of the ALE program, and \(2N\) years is the length of the interval being analyzed. The coefficients \(a_0, b_0, c, d_0,\) and \(s\) are determined optimally by weighting each \(\chi\) by the inverse of the measurement error variance, increased, however, for the autocorrelation time of the residuals [Cunnold et al., 1994]. To evaluate \(a_0, b_0,\) and \(d_0,\) the data are divided into two intervals: one with increasing \(\chi\) (July 1978 to June 1990) and the other with decreasing \(\chi\) (July 1990 to June 1996). The coefficients calculated from the measurements are shown in Table 1. The error bars are calculated in the usual way [e.g., Cunnold et al., 1983] from the residuals with respect to the empirical model fit, increased, however, to account for their autocorrelation.

Between mid-1978 and mid-1990, \(\text{CCL}_4\) increased 1.3 \(\pm 0.1\) ppt yr\(^{-1}\) (or \(-1.3\%\) yr\(^{-1}\), where the uncertainty is the standard error of the four estimates). If the previously described calibration shift is included, the increase over this period would be 1.2% yr\(^{-1}\). These trend values agree with those of Y. Makide (unpublished data, 1991) for this period and differ from our previous estimate (S88) because of the change in absolute calibration. Since mid-1990, \(\text{CCL}_4\) concentrations have decreased \(-0.7 \pm 0.1\%\) yr\(^{-1}\). These annual changes are summarized in Plate 2. The annual increases were relatively uniform up to 1989, and since 1990, the annual decreases have also been relatively uniform. There is typically good consistency between the individual site observations and a model which has been fitted to the observations using transport rates determined from the AGA \(\text{CCL}_3\text{F}\) and \(\text{CCL}_2\text{F}_2\) measurements. The inconsistency in the Mace Head data in 1989–1990 will be discussed in section 5. The average lower tropospheric concentration at the maximum at the end of 1989 was 104.4 \(\pm 3.1\) ppt (based on the uncertainty in absolute calibration). The mean interhemispheric gradient decreased from 4.4 \(\pm 0.2\) ppt in the earlier period of increasing concentrations to 2.5 \(\pm 0.2\) ppt after 1990. The only significant annual cycle terms are those at Samoa, and the amplitude and phase of the variation there are consistent with the annual cycles in the \(\text{CCL}_3\text{F}\) and \(\text{CCL}_2\text{F}_2\)
measurements [see Cunnold et al., 1994] when the different interhemispheric gradients of the species are considered.

4. Emission Estimates

In the work of S88, CCl₄ emissions estimates were based on United States CCl₄ production data tabulated by the U.S. International Trade Commission (ITC) after subtraction of the CCl₄ used in the production of the CFCs. It was pointed out by S88 that a good fit between that emission scenario and the ALE/GAGE data was obtained for a calibration factor of 0.6 applied to the original Rasmussen working standard scale (or 0.74 relative to the OGI 1980 scale by Rasmussen and Lovelock

Plate 1. The monthly mean uncertainties and standard deviations for the CCl₄ measurements at the AGA sites from mid-1978 to mid-1996. Units are dry air mole fractions in parts per trillion (ppt).

Plate 2. Annual increases in CCl₄ estimated from differences between 12-month means at each AGA site (asterisks) and from the best fit two-dimensional model in each semihemisphere of the lower troposphere (solid lines).
The first step is to estimate CC\textsubscript{14} emissions from the production of CC\textsubscript{14} by companies which now report their CFC production values for the United States. Nevertheless, an emission scenario is assembled here based on a procedure similar to that described by S88. It yields approximately the same CC\textsubscript{14} global release estimates up to 1985 and, in addition, provides global release estimates through 1995. The first step is to estimate CC\textsubscript{14} emissions from the production of CC\textsubscript{14} by companies which now report their CFC production to the Alternative Fluorocarbon Environmental Acceptability Study [AFEAS, 1997], the reporting companies. The estimates are based on the calculated releases of CC\textsubscript{14} ratioed to the production used to make the reported CFC production. We emphasize that we are not implying here that the CC\textsubscript{14} releases into the atmosphere mostly occur during CFC production but only that CFC production can provide a good proxy for non-CFC usage of CC\textsubscript{14} and its subsequent release into the atmosphere. Prior to 1986 this ratio is based on the ITC CC\textsubscript{14} and CFC production values for the United States as documented by Simmonds et al. [1988, Table III]. As in the work of S88, the CC\textsubscript{14} not used in the production of CFCs is assumed to be released into the atmosphere within a few months. Figure 3 shows the annual ratio for the United States. Prior to 1972 the ratio varied erratically from year to year but averaged ~17% of the CC\textsubscript{14} used in CFC production. The erratic behavior of the ratio is probably related to inaccuracies in the ITC CC\textsubscript{14} production data exacerbated by the fact that the non-CFC use of CC\textsubscript{14} was a small proportion of the usage in making CFCs. After 1971 the ratio declined primarily because of toxicological concerns about CC\textsubscript{14} usage in the United States. It averaged ~8% from 1972 to 1985. The CC\textsubscript{14} releases derived from Simpson et al. [1988, Table III] have been increased by 2% prior to 1972 and by 1% since that time to roughly account for losses of CC\textsubscript{14} during its production.

Although values for the United States are not available after 1985, an equivalent ratio for the European producers for 1987–1995 may be derived in a somewhat different way. The CC\textsubscript{14} releases into the atmosphere from European sources have been independently estimated from Mace Head pollution events as described by Simmonds et al. [1996] and more recently by Derwent et al. [1998] using trajectory analyses. They showed that there were annual decays in the concentrations of CC\textsubscript{12}F\textsubscript{2}, CH\textsubscript{3}CC\textsubscript{13}, and CC\textsubscript{12}FCC\textsubscript{1}F\textsubscript{2} in the Mace Head pollution events which were roughly similar to the industry-estimated [McCulloch and Midgley, 1998] decay in the European releases of these compounds.

Figure 4a shows the Simmonds et al. [1996] comparison of the industry estimate of CC\textsubscript{12}F\textsubscript{2} releases from Europe against [1983]) combined with an atmospheric lifetime of CC\textsubscript{14} of ~40 years.

Unfortunately, in 1985 the ITC discontinued its practice of supplying CCL\textsubscript{4} production values for the United States. Nevertheless, an emission scenario is assembled here based on a procedure similar to that described by S88. It yields approximately the same CC\textsubscript{14} global release estimates up to 1985 and, in addition, provides global release estimates through 1995. The first step is to estimate CC\textsubscript{14} emissions from the production of CC\textsubscript{14} by companies which now report their CFC production to the Alternative Fluorocarbon Environmental Acceptability Study [AFEAS, 1997], the reporting companies. The estimates are based on the calculated releases of CC\textsubscript{14} ratioed to the production used to make the reported CFC production. We emphasize that we are not implying here that the CC\textsubscript{14} releases into the atmosphere mostly occur during CFC production but only that CFC production can provide a good proxy for non-CFC usage of CC\textsubscript{14} and its subsequent release into the atmosphere. Prior to 1986 this ratio is based on the ITC CC\textsubscript{14} and CFC production values for the United States as documented by Simmonds et al. [1988, Table III]. As in the work of S88, the CC\textsubscript{14} not used in the production of CFCs is assumed to be released into the atmosphere within a few months. Figure 3 shows the annual ratio for the United States. Prior to 1972 the ratio varied erratically from year to year but averaged ~17% of the CC\textsubscript{14} used in CFC production. The erratic behavior of the ratio is probably related to inaccuracies in the ITC CC\textsubscript{14} production data exacerbated by the fact that the non-CFC use of CC\textsubscript{14} was a small proportion of the usage in making CFCs. After 1971 the ratio declined primarily because of toxicological concerns about CC\textsubscript{14} usage in the United States. It averaged ~8% from 1972 to 1985. The CC\textsubscript{14} releases derived from Simpson et al. [1988, Table III] have been increased by 2% prior to 1972 and by 1% since that time to roughly account for losses of CC\textsubscript{14} during its production.

Although values for the United States are not available after 1985, an equivalent ratio for the European producers for 1987–1995 may be derived in a somewhat different way. The CC\textsubscript{14} used in European CFC production during this period may again be estimated stochiometrically from European CFC production values [McCulloch and Midgley, 1998]. The CC\textsubscript{14} releases into the atmosphere from European sources have been independently estimated from Mace Head pollution events as described by Simmonds et al. [1996] and more recently by Derwent et al. [1998] using trajectory analyses. They showed that there were annual decays in the concentrations of CC\textsubscript{12}F\textsubscript{2}, CC\textsubscript{12}F\textsubscript{3}, CH\textsubscript{3}CC\textsubscript{13}, and CC\textsubscript{12}FCC\textsubscript{1}F\textsubscript{2} in the Mace Head pollution events which were roughly similar to the industry-estimated [McCulloch and Midgley, 1998] decay in the European releases of these compounds.

Figure 4a shows the Simmonds et al. [1996] comparison of the industry estimate of CC\textsubscript{12}F\textsubscript{2} releases from Europe against

<table>
<thead>
<tr>
<th>Site</th>
<th>$a_\text{f}$, ppt</th>
<th>$b_\text{f}$, ppt yr$^{-1}$</th>
<th>$d_\text{f}$, ppt yr$^{-2}$</th>
<th>$c_\text{f}$</th>
<th>$s_\text{f}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>July 1978 to June 1990</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adrigole-Mace Head, Ireland, and Cape Meares, Oregon (excluding July 1989 to June 1990)</td>
<td>$100.1 \pm 0.2$</td>
<td>$1.0 \pm 0.1$</td>
<td>$0.09 \pm 0.05$</td>
<td>$-0.2 \pm 0.1$</td>
<td>$1.0 \pm 1$</td>
</tr>
<tr>
<td>Cape Meares, Oregon</td>
<td>$99.9 \pm 0.2$</td>
<td>$1.0 \pm 0.1$</td>
<td>$0.01 \pm 0.06$</td>
<td>$-0.3 \pm 0.1$</td>
<td>$1.0 \pm 1$</td>
</tr>
<tr>
<td>Cape Grim, American Samoa</td>
<td>$94.5 \pm 0.1$</td>
<td>$1.32 \pm 0.03$</td>
<td>$-0.01 \pm 0.02$</td>
<td>$-0.1 \pm 0.1$</td>
<td>$0.3 \pm 0.1$</td>
</tr>
<tr>
<td>Cape Grim, Tasmania</td>
<td>$94.2 \pm 0.1$</td>
<td>$1.33 \pm 0.03$</td>
<td>$-0.02 \pm 0.02$</td>
<td>$0.1 \pm 0.1$</td>
<td>$0.0 \pm 0.1$</td>
</tr>
<tr>
<td><strong>July 1990 to June 1996</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mace Head, Ireland</td>
<td>$103.6 \pm 0.1$</td>
<td>$-0.9 \pm 0.1$</td>
<td>$0.0 \pm 0.1$</td>
<td>$-0.1 \pm 0.2$</td>
<td>$0.1 \pm 0.2$</td>
</tr>
<tr>
<td>Cape Grim, Tasmania</td>
<td>$103.3 \pm 0.1$</td>
<td>$-0.8 \pm 0.1$</td>
<td>$-0.1 \pm 0.1$</td>
<td>$-0.1 \pm 0.1$</td>
<td>$-0.0 \pm 0.1$</td>
</tr>
</tbody>
</table>
| **Figure 3.** The annual CCL\textsubscript{4} releases to the atmosphere expressed as a percentage of the CCL\textsubscript{4} used to produce CCL\textsubscript{13}F\textsubscript{2} and CCL\textsubscript{12}F\textsubscript{2} in the United States based on International Trade Commission values (solid line). The dashed line shows the similar ratio for CCL\textsubscript{4} releases in Europe estimated from polluted air mass measurements at Mace Head and western European production values for the CFCs. The dash-dotted line is a linear fit to the ratio from 1972 to 1995.**

Coefficients were calculated using equation (1). The error bars have been determined from the frequency structure of the residuals for each curve fit; as noted in the text, these error bars might be underestimates because they do not include apparent inconsistencies between the individual site results. Both the Cape Matabula and Cape Meares stations ceased operations at the end of June 1989. Halocarbon measurements were restarted at the Cape Matabula station by the Scripps Institution of Oceanography in January 1992. At Cape Grim, data are missing from July to September 1991 and from May to October 1994. The Adrigole station was shut down from December 1983 to February 1987. Data are restarted at the Cape Matabula station by the Scripps Institution of Oceanography in January 1992. At Cape Grim, data are missing from July to September 1991 and from May to October 1994. The Adrigole station was shut down from December 1983 to February 1987.
the releases estimated from the Mace Head data as well as the estimated emissions from just the reporting countries within Europe. Because there are a number of assumptions that go into deriving the European emissions from Mace Head pollution data including, for example, the extent of vertical mixing during the air parcels' travel from Europe, we have applied a constant adjustment factor to the emissions estimated from the pollution event measurements. Reducing all the estimates by 9% provides the best fit between the combined set of CC13F, CC12F2, CH3CCl5, and CC12F2CCIF2 wind sector derived pollution data and the emission estimates derived from the reporting country data. Here the 1993-1995 results for CC13F were excluded because there is evidence that the standard industry release scenario overestimates the releases during these years [Cunnold et al., 1997].

The CC14 pollution measurements are now used to obtain European CC14 emission estimates (see Figure 4b). These emissions are shown to be well represented by ~4.5% of the CC14 used in the reported regional production of CFCs (Figure 3). The justification for omitting releases from eastern Europe from this paper (they were included by Simmonds et al. [1996]) is not only that estimates of CFC production in eastern Europe are less accurate and our objective is to derive a proxy for CC14 releases in the reporting countries but also that eastern European sources may contribute less to Mace Head pollution events because the western European sources are closer to Mace Head. The implication of Figure 3 is that the ratio of CC14 emissions to the CC14 used in CFC production in reporting countries has undergone a slow decline since 1972, which may be approximated by a linear trend. CC14 releases from all the reporting countries are now estimated using the linear trend in Figure 3 and the reported annual production of the CFCs.

In order to estimate CC14 releases from the nonreporting part of the world using a similar procedure, CFC production there must first be estimated. Estimates were obtained by using the AGA release estimates for the CFCs [Cunnold et al., 1997] and then subtracting the release estimates for the reporting countries (see Table 2). Production from the nonreporting countries was then estimated by multiplying the nonreporting country CFC release estimates by the average ratio of production to releases in the reporting countries over the years 1979-1992 (1.163 for CC13F and 1.045 for CC12F2). Finally, CC14 releases in the nonreporting countries were assumed to be 19% of the CC14 used to make this CFC production, where the 19% value is equal to the average proportion derived from the

### Table 2. World CC14 Releases Inferred Using CFC Production as a Proxy

<table>
<thead>
<tr>
<th>Year</th>
<th>CC14 Used to Make CFCs in Reporting Countries</th>
<th>CC14 Releases From Reporting Countries per Figure 3 Proxy</th>
<th>AGA World Release Estimates</th>
<th>AGA Release Estimates for the Nonreporting Countries</th>
<th>CC14 Used to Make Inferred Rest of World Production</th>
<th>Inferred World CC14 Releases</th>
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<td>23</td>
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Units are 10^3 kg yr^-1. CC14 production in the nonreporting countries has been inferred from Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment/Advanced Global Atmospheric Gases Experiment (AGA) estimates of world CFC releases [Cunnold et al., 1997], assuming that production in the nonreporting countries is 1.163 times CC13F release and 1.045 times the CC12F2 release.
United States ITC values between 1960 and 1971 (with production losses added) before toxicological concerns became prevalent in the United States. For 1993–1995 the above procedure may be invalid because Cunnold et al. [1997] have shown that the CFCs released into the atmosphere by the reporting countries are less than those calculated, although there is no reason to question the reported CFC production values. Therefore the nonreporting country estimates of CFC releases, which are obtained by subtraction (see Table 2), are unreliable for these years. The nonreporting country releases of CCl₄ for 1993–1995 have therefore been assumed to be equal to the average of the releases for 1988–1992. The estimated global emissions of CCl₄ are shown in Table 2, together with a summary of the calculations used to arrive at these emission estimates. The emission estimates are also indicated in Figure 5.

5. Comparison Between the CCl₄ Emission Scenario and the AGA Measurements

Figure 5 compares the CFC proxy estimates for CCl₄ releases against the global CCl₄ emissions estimated from the AGA CCl₄ measurements. The AGA-derived CCl₄ emission estimates are based primarily on the measured globally averaged change in the 12-month-smoothed CCl₄ concentrations from 1 year to the next combined with a 12-box two-dimensional model of the atmosphere, which is used to simulate upper tropospheric and stratospheric inventory changes [Cunnold et al., 1994]. The CCl₄ equilibrium lifetime assumed in these calculations was 42 years, which is the midpoint of the photochemical model estimates of 30–54 years cited by Ko and Jackman [1994]. The assumed distribution of loss rates in the four stratospheric boxes came from a recent run of the Golombek and Prinn [1986] three-dimensional model using updated rate coefficients.

Figure 5 also shows the pre-1986 emission estimates from the emission scenario given by S88. This scenario is seen to be not significantly different from the one used in this paper. The differences shown in Figure 5 primarily reflect the straight-line fit (Figure 3) used here versus the actual annual values, which were used by S88. The 12-month-smoothed estimated atmospheric inventory of CCl₄ at the end of 1978 is 2290 × 10⁶ kg, which may be compared against an inventory of 2230 × 10⁶ kg estimated from the emission scenario by S88 for a lifetime of 42 years.

In Figure 6 the model using the AGA-derived emissions and a 42-year lifetime is shown to simulate the measurements well.
Figure 5 shows the differences between the northern hemisphere (NH) semihemisphere values and the southern hemisphere averages. For the northernmost semihemisphere the measured differences are well simulated by the two-dimensional model after 1984, following the termination of measurements at Adrigole, Ireland; the absence of the effects of the high concentrations noted in section 5 over Ireland in 1989 and 1990 occurs only because there were no measurements at Samoa at that time and the southern hemisphere means were therefore not calculated. The model provides a good simulation of the annual series of differences between the Oregon and post-1990 Mace Head measurements and the southern hemisphere concentrations.

Figure 8b shows the Barbados-southern hemisphere (SH) differences. Although the model simulates the change in gradient in 1990, the gradient is being persistently underpredicted by the model. CC\textsubscript{14} is the only one of five chlorocarbons (the others being three CFCs and methyl chloroform) simulated in this way, which exhibits a persistent, one-sided difference in the gradient. The model calculations assumed that ~90% of the emissions occurred in the northernmost semihemisphere based on similarities between the technology and uses of CC\textsubscript{14} and those of the other chlorinated gases measured by AGA (for which some sales distribution values are available). Because of the inferred dominance of the sources of CC\textsubscript{14} from nonreporting countries, in the past few years, this latitudinal gradient has been interpreted as being due to non-CFC production usage of CC\textsubscript{14}.

It is useful to evaluate how well the transport model simulates the latitudinal gradient of CC\textsubscript{14} and, in particular, how well it mirrors the sudden drop in the emissions around 1990. The absence of discontinuities in Figure 6 confirms the model's ability to simulate the sudden change in the emissions. However, it is better illustrated by considering the time series of the annual mean differences between some of the sites. Figure 8a shows the differences between the northern hemisphere (NH) semihemisphere values and the southern hemisphere averages.

However, it is evident that the poorest fit is with the pre-1991 measurements in Ireland. This apparent inconsistency between these Irish measurements and those at the other sites is obvious in Plates 1 and 2. It has been suggested in the past that this might be associated with large emissions from eastern Europe and the former USSR [Simmonds et al., 1983; Prather, 1985, 1988]. Alternatively, the obvious variability of the record pre-1991 suggests that persistent local contamination or measurement difficulties may be the cause of this inconsistency (these features are not present in the time series of any other species). Whatever the cause, it would appear that the pre-1991 CC\textsubscript{14} data from Ireland are probably not typical of the semihemisphere, and conversely, it may be noted that the data from Oregon are well simulated by the model and hence are more consistent with the data from the other sites. The annual release estimates have therefore been recalculated with the pre-1991 data from Ireland excluded. The results of this calculation have also been included in Figure 5. The main effects are to delay the sharp drop in the emissions from 1990 to 1991 and to remove the spike in the emissions in 1989.

It is evident from the magnitude of the error bars in Figure 5 that year-to-year variations (i.e., the high-frequency variability) in the CC\textsubscript{14} emissions are not statistically significant. Because the uncertainties in the emission estimates decrease rapidly when the estimates are smoothed over periods longer than a year, it is useful to show the smoothed emission estimates. For example, for emissions averaged over 2-year periods the error bars decrease by almost a factor of 3. We have utilized an optimal smoother in which the individual year measurements are weighted in proportion to the inverse square of the standard deviation of the residuals. The effective smoothing time is between 2 and 3 years. These smoothed emission estimates are shown in Figure 7. For comparison, the same smoothing has also been applied to the CFC proxy release scenario values.

Figure 7 also shows the results of adjusting the measurements for the possible shift, discussed in section 2.2, in the calibration of 1.5% between 1984 and 1988. This causes a small decrease in the estimated emissions (by a total of 28 x 10\textsuperscript{6} kg).

From Figures 5 and 7 it is concluded that global emissions of CC\textsubscript{14} averaged 94 x 10\textsuperscript{6} kg yr\textsuperscript{-1} from 1979 to 1990 and that they averaged 49 x 10\textsuperscript{6} kg yr\textsuperscript{-1} from 1991 to 1995. The proposed release scenario provides a good fit to the inferred releases except that the values are ~10% too small. This discrepancy would be removed if the CC\textsubscript{14} lifetime is 47 years. The emission scenario suggests that releases from the reporting countries decreased to <10 x 10\textsuperscript{6} kg yr\textsuperscript{-1} in 1995 from ~60 x 10\textsuperscript{6} kg yr\textsuperscript{-1} ~15 years earlier. On the other hand, the CC\textsubscript{14} emissions from countries which do not report their CFC production to AFEAS are inferred to have remained approximately constant at 30 x 10\textsuperscript{6} kg yr\textsuperscript{-1}. Since this number is much larger than the estimated reporting country emissions of CC\textsubscript{14} we infer that global CC\textsubscript{14} emissions, and hence the downward trend in atmospheric CC\textsubscript{14} of ~0.7 ppt yr\textsuperscript{-1}, are likely to remain approximately constant until restrictions on CC\textsubscript{14} (and CFC) production in the developing countries begin to apply early in the next century (50% phaseout by 2005, 85% by 2007, and 100% by 2010). We are also inferring that in 1995, although production of CFCs by reporting and nonreporting countries was approximately equal, the emissions of CC\textsubscript{14} into the atmosphere were ~3 times larger from the nonreporting countries than from the reporting countries because of their much greater, non-CFC production usage of CC\textsubscript{14}.
the two NH semihemispheres. Clearly, such a redistribution of the emissions does little to explain the poor simulation of the Barbados–SH differences.

Another possible explanation is that 1 ppt is approximately the accuracy of the ALE/GAGE CC\(_4\) measurements. For example, when the AGAGE HP5890 began to operate at Barbados in July 1996, the measured concentrations decreased by ~0.5 ppt. The introduction of the new HP5890 considerably improved the chromatographic resolution between methyl chloroform and carbon tetrachloride compared with the older HP5880 instrument. This resulted in more accurate peak integration and might account for a small measurement bias in the older instrument. The Climate Monitoring and Diagnostics Laboratory (CMDL) CC\(_4\) in situ gas chromatograph measurements at Mauna Loa [e.g., Montzka et al., 1996] were also examined. For CC\(_3\)F the measurements at Mauna Loa and Barbados exhibit similar concentrations when the absolute calibration differences are considered. The CMDL CC\(_4\) measurements possess an absolute calibration difference of ~3% (CMDL is higher), and after accounting for this the Barbados measurements are found to be ~1 ppt higher than the Mauna Loa values. An independent check on the accuracy of the ALE/GAGE observations is obtained by examining the Samoa-Tasmania differences. The standard deviation of the annual differences about the model-simulated differences of <1 ppt is 0.6 ppt. The correlation time of these annual mean differences is 3–4 years. An example of this is seen in Table 1, where the mean difference between Samoa and Tasmanian changes, for no obvious physical reason, from 0.3 ppt in the 1978–1990 period to 1.3 ppt in the 1990–1996 period. Therefore we consider that ALE/GAGE CC\(_4\) measurements have an accuracy of 0.6 ppt (one standard deviation) at each site. Such an accuracy is insufficient for us to be able to infer anything significant about the latitudinal distribution of the CC\(_4\) emissions at this time. However, the AGAGE measurements are expected to provide both a significant improvement in accuracy and better maintenance of this accuracy over a number of years of observations.

All the model calculations and the emission estimates in section 5 have been made using an assumed CC\(_4\) lifetime of 42 years. There are, however, two sets of observations which suggest a shorter lifetime. From measurements of CC\(_4\) in the lower stratosphere and correlations against other long-lived gases, Volk et al. [1997] have inferred a lifetime of 32 ± 6 years. Furthermore, Butler et al. [1993] have shown that the oceans are 5–7% undersaturated in CC\(_4\), and they have inferred a flux to the ocean of 1 nmol m\(^{-2}\) d\(^{-1}\), which equates to a sink that in isolation would lead to a lifetime of ~200 years. Also, the updated runs of the three-dimensional model of Golombek and Prinn [1986] as reported by Ko and Jackman [1994] imply a steady state lifetime of 29 years.

A combined atmosphere and ocean lifetime of 30 years would increase all of our CC\(_4\) emission estimates derived from the AGA data by ~23 × 10\(^6\) kg yr\(^{-1}\) and would imply 13% larger emissions prior to 1979. In our emissions scenario the reporting country emission estimates were based on industry-derived sales values for the United States and emission values for Europe, in which there are no obvious errors. Instead, in order to account for the increased emissions in the release scenario, we would suggest a change in the nonreporting country emissions because these are more poorly known. Then ~35% of the CC\(_4\) used to make the inferred production of CFCs in the nonreporting countries would have to be released annually. The increased emissions would result in an increase in the modeled Barbados—southern hemisphere gradient by ~0.7 ppt (an improved simulation) but would also increase the modeled northernmost semihemisphere—southern hemisphere gradient by ~1 ppt (yielding a worse simulation after 1985). Neither the AGA measurements nor the recently released United Nations Environment Programme (UNEP) [1997] tabulation of global CC\(_4\) production and consumption (because of year-to-year variabilities and possible inconsistencies) provide a way to decide which set of emissions is correct and whether the CC\(_4\) lifetime is 30 or 42 years.

6. Conclusions

CC\(_4\) measurements, several times per day, from July 1978 to June 1996 at five remote surface sites of the ALE/GAGE/AGAGE network have been reported. The SIO 1993 calibra-
tion scale is used, which reduces concentrations by a factor of 0.77 relative to previous ALE/GAGE CCl₄ reported measurements [Simmonds et al., 1988]. The measurements indicate that CCl₄ increased fairly uniformly at an average rate of 1.3 ± 0.1 ppt yr⁻¹ from 1978 to 1990 and that since 1990, concentrations have decreased fairly uniformly by 0.7 ± 0.1 ppt yr⁻¹. The maximum globally averaged concentration in the lower troposphere occurred in 1990 at 10±4 ± 3.1 ppt with the uncertainty being largely associated with residual uncertainties in the absolute calibration scale.

Global emission estimates have been calculated from these measurements. Assuming an atmospheric lifetime for CCl₄ of 42 ± 12 years, global emissions from 1979 to 1988 averaged 94.5 ± 11 and 49.7 ± 16 x 10⁶ kg yr⁻¹ from 1991 to 1995. On the basis of the 42-year lifetime and these emission estimates, the temporal evolution of the interhemispheric gradient of CCl₄ for the northernmost semihemisphere was found to be well simulated provided that measurements in Ireland prior to 1991 were assumed to be atypical of that semihemisphere. On the other hand, a better simulation of the Barbados-southern hemisphere gradient is provided by assuming a CCl₄ lifetime of 30 years. The accuracy of the measurements at individual sites may only be ~0.6 ppt, which is inadequate for providing a constraint on the atmospheric lifetime of CCl₄ based on the measured latitudinal gradient.

The estimated emissions show a sharp decrease in 1990–1991. This is coincident with decreases in the global production of CCl₃F and CCl₂F₂ for which CCl₄ is the feedstock. This provides support to the idea [Simmonds et al., 1983, 1988] that CFC production is a good proxy for CCl₄ releases into the atmosphere. In this paper the CCl₄ release scenario from Simmonds et al. [1988] has been slightly modified and extended from 1985 to 1995. It has been shown that the CCl₄ emissions from countries which report CFC production values have declined from an amount equivalent to ~11% in 1972 to ~4% in 1995 of the CCl₄ used to manufacture the reported CFC production. For the nonreporting part of the world it was assumed that 19% of the CCl₄ used in CFC production is being emitted. (This percentage was characteristic of the United States prior to 1972). This release scenario yields a 3% underprediction of the measured atmospheric inventory of CCl₄ on July 1, 1978, and it yields emissions which average 86 x 10⁶ kg yr⁻¹ from 1979 to 1989 and 39 ± 10⁶ kg yr⁻¹ from 1991 to 1995. This would agree with the ALE/GAGE/GAGE emissions estimated from the measurements if the atmospheric lifetime of CCl₄ were to be ~47 years, but the scenario would underestimate the inferred releases by ~30 x 10⁶ kg yr⁻¹ if the atmospheric lifetime were 30 years. In either case we infer that the nonreporting countries must be making substantial contributions to the worldwide emissions of CCl₄ and that since 1990, the releases from those countries probably have exceeded the releases by the reporting countries, probably because of additional, non-CFC production uses for CCl₄.

Acknowledgments. This research was supported by NASA grants NAGW-732 (R. Prinn, D. Cunnold, F. Alyea, P. Fraser, P. Simmonds, and S. O’Doherty), NAGW-2034 (R. Weiss), and NAG1-1805 (R. Prinn); Chemical Manufacturers Association contracts FC-85-567 and FC-85-568 (P. Simmonds); DOE (U.K.) contract PEC 7/10/54 (P. Simmonds); SPA-AFEAS grant CTR92/P02-008 (P. Fraser and R. Prinn); CSIRO, Aspendale, Victoria, Australia (P. Fraser); and the Bureau of Meteorology, Melbourne, Victoria, Australia (P. Fraser). Valuable local support at the ALE/GAGE stations and supporting laboratories was provided by G. Spain and D. Brown (Mace Head, Ireland); P. Sealy (Ragged Point, Barbados); Chris Harth, Mark Winney, and the NOAA staff (Cape Matatula, Samoa) and P. Steele, N. Duck, and M. Lucarelli (OCEANO). We also acknowledge the substantial contributions to the ALE/GAGE measurements prior to 1990 by R. Rasmussen and A. Crawford (OGI).

References


