GAGE/AGAGE measurements indicating reductions in global emissions of CCl$_3$F and CCl$_2$F$_2$ in 1992–1994

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Abstract. Global Atmospheric Gases Experiment/Advanced GAGE (GAGE/AGAGE) observations of CCl$_3$F indicate that global concentrations of this compound reached a maximum in 1993 and decayed slightly in 1994; CCl$_2$F$_2$ concentrations increased approximately 7 ppt in both 1993 and 1994. The observations suggest that world emissions in these two years were smaller than industry production figures would suggest and have decreased faster than expected under the Montreal Protocol and its amendments. An analysis of regional pollution events at the Mace Head site suggest that industry may be underestimating the decline of emissions in Europe. It is argued, however, that the decline in European emissions is not biasing the background Mace Head measurements (or the GAGE global averages). Combining the chlorofluorocarbon measurements, including CCl$_2$FCCl$_2$F$_2$, with GAGE/AGAGE measured global decreases in CH$_3$CCl$_3$ and CCl$_4$ after 1992 and with Cape Grim archived air measurements of CHClF$_2$, the measurements suggest that anthropogenic atmospheric chlorine loading from these six gases maximized in 1992 at 2.95 ± 0.04 ppb and that it had decreased by 0.02 ± 0.01 ppb by the beginning of 1995.

1. Introduction

As a result of the Montreal Protocol [World Meteorological Organization (WMO), 1988] (and its subsequent modifications, United Nations Environment Program (UNEP), 1992), the global production of chlorofluorocarbons and chlorocarbons has declined dramatically since 1990 [e.g., Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), 1996]. This production decline has resulted in substantial reductions in the annual rates of increase of these gases in the atmosphere [e.g., Elkins et al., 1993; Simmonds et al., 1993; Cunnold et al., 1994; Fraser et al., 1996] and because of its much shorter lifetime in a decrease in 1, 1, 1-trichloroethane (CH$_3$CCl$_3$) since 1992 [Prinn et al., 1995]. The Global Atmospheric Gases Experiment (GAGE) and Advanced GAGE (AGAGE) measurements of these gases have documented these changes and these measurements can be used to infer the emission rates of these gases into the atmosphere [e.g., Cunnold et al., 1994; Fraser et al., 1996]. The emission estimates can be used as an indirect test of compliance with the Montreal Protocol based on comparisons against the industry emission estimates derived from the production figures. These figures can also be used to assess the emissions by nonreporting companies and/or changes in patterns of global usage. The Montreal Protocol restricts production of a combined group of chlorinated compounds, and the compounds being measured by GAGE/AGAGE contribute the largest part of the global atmospheric chlorine input and particularly its annually changing component. The measurements therefore provide estimates of the rate of increase of chlorine in the troposphere (the chlorine loading [cf. Prather et al., 1996]). Changes in tropospheric chlorine are important for predicting future levels of stratospheric ozone destruction and changes in atmospheric halocarbon concentrations affect the global warming potential. In this paper, recent GAGE/AGAGE measurements of CFC-11 (CCl$_3$F) and CFC-12 (CCl$_2$F$_2$) through mid-1995 are emphasized in the analysis, and some limited comparisons are included against the concentrations measured by the National Oceanic and Atmospheric Administration (NOAA), Climate Monitoring and Diagnostics Laboratory (CMDL) through 1993 from flask samples. In addition, the measurements are used to determine the global emissions.

2. GAGE/AGAGE Measurements of the Atmospheric Accumulation of Chlorofluorocarbons

Simultaneous Atmospheric Lifetime Experiment (ALE)/GAGE measurements of CCl$_3$F, CCl$_2$F$_2$, CH$_3$CCl carbon tetrachloride (CCl$_4$), and nitrous oxide (N$_2$O) have been made, 12 times per day (for GAGE), at four or five remote ground-based sites (Adrigole/Mace Head, Ireland; Cape Meares, Oregon (until 1989); Ragged Point, Barbados; Cape Matatula, Samoa; Cape Grim, Tasmania) continuously, with minor exceptions, since mid-1978. Measurements of CFC-113 (CCl$_2$FCClF$_2$) and methane (CH$_4$) were added in approximately 1985. More recently, new AGAGE instruments replaced the HP5880s at Mace Head in February 1994 and in August 1993 at Cape Grim. The AGAGE instrument is a
modified HP5890 incorporating many improvements, resulting in increased precisions for most species (better than 0.1% for CCl$_3$F and CCl$_2$F$_2$). The instrument includes an internal measurement of nonlinearity, obtained utilizing programmed injections of the calibration gas at a series of superambient and subambient pressures, so that adjustments can be applied to each measured concentration. AGAGE provides approximately 30 ambient measurements per day. This paper concentrates on the CCl$_3$F and CCl$_2$F$_2$ measurements because these two species make the largest anthropogenic contributions to the chlorine loading of the atmosphere. There has been a substantial reduction in their rate of accumulation in the atmosphere in the past few years.

Atmospheric Lifetime Experiment (ALE) and GAGE measurements prior to mid-1991 have been reported by Cunnold et al. [1994] (hereinafter referred to as C94). In this paper the following four years of measurements (through mid-1995) are emphasized. In C94 the measurements were reported on the Scripps Institution of Oceanography (SIO, 1993) absolute calibration scale, with the best available scale factor for converting from the original ALE/GAGE calibration scale to the SIO 1993 scale being based on measurements of six secondary calibration standards at both Cape Grim and SIO. Additional measurements of these and four other standards since that time have resulted in small changes in the scale conversion factors. The factors for converting from the SIO 1993 scale to the OGI 1980 scale are now 1.050 (versus 1.055 in Table 1 of C94) for CCl$_3$F and 0.963 (versus 0.962) for CCl$_2$F$_2$.

The time series of the CCl$_3$F and CCl$_2$F$_2$ concentrations are shown in Plates 1a and 1b. AGAGE measurements started at Mace Head in February 1994 and at Cape Grim in August 1993. GAGE measurements continued for several months in order to provide an overlap period and stopped at these sites in June and December 1994, respectively. AGAGE and GAGE monthly means have been averaged in Plate 1, and the standard deviations have been combined. Note the slightly smaller standard deviations in AGAGE at Mace Head due perhaps to improved instrumental precision and better resolution of pollution events.

Plate 1. (opposite) Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment/Advanced GAGE (ALE/GAGE/AGAGE) (a) CCl$_3$F and (b) CCl$_2$F$_2$ monthly means (in the Scripps Institution of Oceanography (SIO) 1993 calibration scale) and standard deviations at Adrigole/Mace Head, Ireland; Cape Meares, Oregon; Ragged Point, Barbados; Cape Matatula, Samoa; and Cape Grim, Tasmania.
The annual release estimates and error bars have been joined by solid lines to make the trends more evident. Also shown are the industry estimates of Reporting Company (dots) and world (dashed lines joining crosses) releases. The emission levels for the 5-year period, 1990–1994, from the 1982 scenario [Prather et al., 1996] are denoted by MP-11 and MP-12.

Figure 1. Releases of CFC-11 (CCl$_3$F) and CFC-12 (CCl$_2$F$_2$) in each calendar year estimated from the ALE/GAGE/AGAGE measurements using lifetimes of 50 years for CCl$_3$F and 110 years for CCl$_2$F$_2$. The annual release estimates and error bars have been joined by solid lines to make the trends more evident. Also shown are the industry estimates of Reporting Company (dots) and world (dashed lines joining crosses) releases. The emission levels for the 5-year period, 1990–1994, from the 1982 scenario [Prather et al., 1996] are denoted by MP-11 and MP-12.

Plate 2 shows that the atmospheric increases in CCl$_3$F and CCl$_2$F$_2$ were fairly constant (approximately 9 and 17 ppt/year, respectively) from 1979 to 1984. The rate of increase was larger in the 1984–1987 period just prior to the global consumption constraints of the Montreal Protocol. Since 1987 for CCl$_3$F and since 1988 for CCl$_2$F$_2$, the annual increases of each compound have declined dramatically. The measurements have shown no significant change in CCl$_3$F in the atmosphere from 1992 onward. In contrast, the atmospheric concentrations of CCl$_2$F$_2$ still increased approximately 7 ppt in both 1993 and 1994 (as a result, we propose a longer lag between sales/production and release for most of the uses of CCl$_3$F).

If the two-dimensional model is run in the mode of determining the atmospheric lifetime of these gases, based on the observed inventories and trends together with the emission estimates tabulated by the industry [e.g., AFEAS, 1996], steady state lifetimes of 52±23 years for CCl$_3$F and 172±416 years for CCl$_2$F$_2$ are calculated (the calculation procedure and the error bars are similar to those described in C94); the lifetime estimates derived from the trends alone, which have smaller error bars, are 47±9 years for CCl$_3$F and 135±32 years for CCl$_2$F$_2$. The inventory lifetime estimates have some sensitivity to the transport time from the troposphere to the stratosphere. In C94 a

[Figure 2. Ratios of measured CCl$_3$F and CCl$_2$F$_2$ mixing ratios in primary standard R-363 (diamonds), as well as R-363 proxies (G-003 (circles), G-008 (squares), and G-025 (triangles)) to measured CCl$_3$F and CCl$_2$F$_2$ mixing ratios in primary standard R-382. These five tanks were/are stored at Cape Grim and were/are used to assign mixing ratios to the secondary standards used in the field from 1990 to 1995. The lines are linear regressions to the respective ratios and the slope term and their uncertainties are -3.787 (±2.06) x 10^-4 (CCl$_3$F) and-3.053 (±1.36) x 10^-4 (CCl$_2$F$_2$). This means that there is a 95% chance that over the 6 years that these tanks have been used to calibrate secondary standards, the drifts of CCl$_3$F and CCl$_2$F$_2$ in the tanks relative to any drift in R-382 are less than 0.2 ppt/yr and 0.3 ppt/yr, respectively.]
transport time of 3 years was assumed; however, in more recent comparisons against other two-dimensional models [Prinn et al., 1995], the average value of this transport time in the models is 2 years. In the interest of maintaining consistency with these other models and with the CH₂Cl₂ calculations by Prinn et al. [1995], we have now adopted a transport time of 2 years between 350 and 100 mbar with an uncertainty of ±1 year. This change in transport time together with the minor changes in lifetime values noted earlier are responsible for the small changes in lifetime versus C94. The lifetime estimate for CC13F is now remarkably similar to that estimated from models based upon the measured absorption cross section for this gas [Ko and Jackman, 1994]. For CC12F₂ the lifetime discrepancy between the measurements (172 years) and the models (110 years) remains. In C94 this difference was ascribed in part to underestimate of the releases by nonreporting companies and shorter time differences between sales/production and release compared with the industry estimates [e.g., Gamlen et al., 1986].

3. Atmospheric Releases of CC13F and CC12F₂

As in C94 annual estimates of releases may be calculated from the ALE/GAGE/AGAGE measurements (hereafter abbreviated as just the AGA measurements) based on assuming atmospheric lifetimes for the chlorofluorocarbons. In these calculations, the model/measured absorption cross-section based steady-state lifetime values of 50 years for CC13F and 110 years for CC12F₂ have been adopted [Ko and Jackman, 1994]. The resulting annual emission estimates are compared against the industry estimates [AFAES, 1996; Fisher et al., 1994] in Figure 1. Note, however, that for 1993 and 1994, industry has only provided reporting company values, the depicted global emissions include nonreporting company values for those years equal to the 1992 values. P. Midgley (M&D Consulting, Leinfelden, Musberg, Germany) suggests that this is a reasonable assumption. Note that the error bars on the ALE/GAGE/AGAGE (AGA) estimates after 1989 are less than those on the earlier estimates as a result of the improved consistency of secondary calibration after 1990, which was described in section 2. Figure 1 also shows the projected levels based on the Montreal Protocol which are reported as 5-year averages in the IS92 scenarios by Prather et al. [1996]. Both the emission estimates by industry and the emission estimates derived from the AGA measurements are clearly lower than the projected levels. This suggests that the Montreal Protocol has been successful in reducing worldwide emissions of CC13F and CC12F₂ and that the phaseout of the emissions is proceeding somewhat faster than was projected.

For CC13F there is excellent agreement between the industry and the AGA emission estimates until 1993. The disagreement between the emission estimates in 1993 and 1994 is not easily accounted for, particularly when it is assumed that the production by the reporting companies is accurately known. The substantial drop in the emissions is not explained by either a redistribution of the emissions between open and closed cell foams or changing the residence time in closed cell foams. Ko and Jackman [1994] report uncertainties of approximately 10 years in the model-derived lifetime estimates for both CC13F and CC12F₂. This uncertainty can result in systematically larger or smaller emission estimates (by approximately 20 × 10⁶ kg for CC13F after 1989), but it would have little effect on the downward trend in the estimated emissions after 1988. We are forced to conclude either that recent global production is not being released to the atmosphere as fast as it was in the past, perhaps because of recent conservation measures or stockpiling, or that emissions (and production) by nonreporting companies have declined more dramatically than those resulting from the production by the reporting companies.

The CC12F₂ measurements consistently yield larger release rates up to 1989 than the estimates based on production [Fisher et al., 1994] by approximately 30 × 10⁶ kg/yr and the accumulated releases prior to 1979 inferred from the measurements are approximately 3% larger than the estimates derived from the production figures. A combination of measurement and modeling uncertainties, such as a reduction in the release time in the nonhermetically sealed usage from 4 to 3 years, which could account for roughly one third of this discrepancy (and provide better agreement in the logarithmic trends), together with some increase in releases (e.g., 20%) by the nonreporting companies could explain this discrepancy. However, just as was the case for CFC-11, none of these changes can account for the large decline in the releases estimated from the measurements in 1992-1994. Again the measurements imply either that production by the nonreporting companies has recently declined more dramatically than that by the reporting companies or that production is being released to the atmosphere less rapidly into the production figures. The same conclusion was reached for CC1₂F₃ emissions [Fraser et al., 1996].

4. European Emission Reductions and the Representativeness of Mace Head

The reason that this question should be considered is that the recent substantial decreases in the CFC releases are expected to have been accompanied by some spatial redistribution in the releases. For example, on the basis of production/sales figures, Simmonds et al. [1996] have indicated that the CC1₂F₃ emissions from Europe declined 65% between 1987 and 1993 and that the proportion of the reporting company releases coming from Europe decreased from 39 to 22% over this same period. This might have altered the representativeness of Mace Head for the northernmost semihemisphere. This question is addressed in several ways in the following paragraphs:

It is well recognized that large, short-duration increases in the concentrations of chlorofluorocarbons and 1,1,1-trichloroethane observed at Mace Head are produced by the arrival of regionally polluted air masses from Europe [Simmonds et al., 1993, 1996]. These events have been used to provide estimates of the European emissions of these gases and their temporal variation [see also Prather, 1988]. Using trajectory analysis and assuming that the emissions get uniformly distributed rapidly over a boundary layer depth of 800 m, Simmonds et al. [1996] have produced annual emission estimates for CC1₂F₃ and CC1₂F₂ (as well as for the other GAGE gases) from Europe which agree with the production- and sales-derived estimates within a factor of 2-3. For purposes of this paper, however, it is the inferred trend in the emissions which is particularly relevant: Simmonds et al. [1996] have shown that on the basis of the GAGE measurements and the trajectory approach, European emissions between 1987 and 1994 apparently declined by almost a factor of 10 for CC1₂F₃ (versus a factor of 2.5 from the production/sales approach) and by a factor of 6 for CC1₂F₂ (versus a factor of approximately 4 from the production/sales approach).
April to June and October to December measurements (dashes and bottom solid line is a fit to the average of the tenth to 25th)

This approach almost entirely avoids the potential analysis problem that in recent years the number of detectable pollutants has declined significantly (also see Figure 3). Figure 3 shows the results of sorting pollution events at Mace Head, Ireland. The top solid line is a fit to the average of the fifth to fifteenth largest events during individual months (the selected event range was, however, proportionately reduced for months with missing data) and then averaged over the months April to June and October to December. The bottom solid line is a fit to the average of the tenth to 25th largest events (and the individual annual values are indicated by pluses). Also shown are the average percentage of events which are detectably polluted over these periods (dashes and three dots) and the European emission level estimates reported by Simmonds et al. [1996] based on production figures (these are indicated by the dashed line and are expressed in global ppt emission levels per 10 years). The numbers on the left-hand ordinates apply to all the curves.

A somewhat simpler procedure for estimating the trend in European emissions from the Mace Head pollution data gives similar results. Figure 3 shows the results of sorting pollution events by magnitude during each month and of determining the average, for example, over a fraction of the largest events. This approach almost entirely avoids the potential analysis problem that in recent years the number of detectable pollution events has declined significantly (also see Figure 3). Figure 3 shows the decline in the emissions based on the combined April to June and October to December measurements (during the other months there were usually insufficiently few pollution events). From 1987 to 1994 the implied European emissions have declined by approximately a factor of 12 for CCl3F and a factor of 7 for CCl2F2. Although nonlinearity is only fully accounted for with the new AGAGE instrumentation, it is significant that both the GAGE silicone and the porasil channel measurements of CCl3F have shown similar declines. The similarity of the declines at the two different pollution levels (shown by the two curves in Figures 3a and 3b) also indicates that nonlinearities are not a major factor in the decline. Only GAGE measurements were used in constructing Figure 3 in order to avoid any possible problem related to different sampling frequencies in ALE, GAGE, and AGAGE. Comparisons of the Figure 3 values against similarly derived values for Adrigole, Ireland, in ALE before 1985 (but reducing the selected event range in proportion to the fewer monthly measurement in ALE) exhibit a similar proportion of polluted events to those in 1987–1989 but indicate that 1987 may have contained an exceptionally large number of strong pollution events.

The substantial differences between the trends in the production/sales estimates of the emissions from Europe and those derived from pollution events at Mace Head are not easily explained. The rapid decline in pollution levels is more consistent with the decline in the very short-lived uses of the CFCs (i.e., aerosols) which accounted for approximately one half of the global releases in 1987. The magnitude of the pollution events at Mace Head are highly variable from one hour to the next, and it would not be surprising if this variability were to be caused not only by spatial variability in the emissions but also by temporal variability. Any such temporal variability is almost certainly due to rapid release uses and immediate release during the production of the products and not due to the steadier releases from closed-cell foams and hermetically sealed refrigerators. Thus an analysis which selectively looks at the larger-amplitude pollution events could be emphasizing short-lived uses, but it would not explain the results of Simmonds et al. [1996]. It is interesting that a similar analysis applied to the Cape Grim, Tasmania, pollution events shows a similarly rapid decline in their amplitude. For purposes of this paper, the relevant result is that the production of the global emissions coming from Europe might have declined more than the production/sales figures indicate and by up to a factor of 4.

Three-dimensional model calculations can provide an estimate of the concentration changes at each measurement site produced by changes in the global distribution of releases. Two relevant runs of the Community Climate Model (CCM2) at the National Center for Atmospheric Research (NCAR) model, which produces a good simulation of the observed latitudinal gradient, have recently been reported [Harley et al., 1996]. These two runs utilized the release distributions for CCl3F illustrated in Figure 4 which are based on two different ways of estimating the releases. The Hartley and Prinn [1993] estimates (hereinafter referred to as HP) yield (western) European releases which are approximately one half of the more directly inferred estimates by McCulloch et al. [1994] (hereinafter referred to as MMF). Individual site differences between the two runs therefore provide an estimate of the effect of changing the proportion of the releases coming from Europe by approximately a factor of 2 (for an annual emission rate of $345 \times 10^6$ kg). Table 1 shows the comparison of the annual-mean concentrations at the AGA sampling sites predicted by the CCM2 for the two release scenarios. Table 1 first shows that the concentrations in the four semihemispheric boxes differ by 0.4, 0.0, 0.1, and 0.2%, respectively, going from north to south for the two emission scenarios; this change is well simulated by...
the two-dimensional model which shows differences of 0.4, 0.0, −0.2, and −0.2%.

The CCM2 calculations cannot be used to directly resolve the effects of changes in the emission distributions between 1987 and 1993/1994 because they do not include the overall reduction in global emissions over this period. Calculations with the two-dimensional model show that year-by-year differences between the concentrations in the two northern hemisphere semihemispheres over this period are directly proportional to the year-by-year differences between the emissions from western Europe and the emissions from the other areas which are located in the northernmost semihemisphere. It is therefore assumed that the differences between the two runs shown in Table 1 are directly proportional to the differences between the emissions from western Europe and the emissions from the other areas which are located in the northernmost semihemisphere. The Table 1 differences then correspond to a change in western European CCl3F releases of approximately 130 × 10^6 kg/yr. The 1994 releases of CCl3F from western Europe are 20–60 × 10^6 kg (Simmonds et al. [1996], depending on whether the estimate is based on the industry estimate or that from pollution measurements), and the total release in the northernmost semihemisphere is approximately 0.83 × 134 × 10^6 kg (from AGA), equal to 111 × 10^6 kg. Therefore the contrast in the CCl3F emissions is at most 90 × 10^6 kg (i.e., 0.7 times the emission distribution differences in the CCM2 runs) and approximately 180 × 10^6 kg for CC12F2 (1.4 times the emission differences).

On this basis the CCM2 results indicate that the representativeness of Mace Head for the northernmost semihemisphere, based on the difference between the column 4 value for the semihemisphere and the column 4 values for the individual sites, has changed between 1987 and 1994 by less than 1 ppt for both CCl3F and CC12F2. Specifically, the CCM2 results suggest that the average of Mace Head and Cape Meares (or Mace Head alone) might have changed its representativeness over this period by less than 0.3 ppt for CCl3F and 0.6 ppt for CC12F2.

Table 1 also shows the calculations at locations in the northernmost semihemisphere (Barrow, Alaska, 71°N, 157°W and Niwot Ridge, Colorado, 40°N, 105°W) where flask samples have been collected routinely since 1977 by the Climate Monitoring and Diagnostics Laboratory (CMDL) of the National Oceanic and Atmospheric Administration (NOAA) [Elkins et al., 1993]. Comparisons of the AGA measurements against the publicly available flask sample time series from 1987 to 1993 provide a second test and some support for the representativeness of Mace Head. To establish a basis of comparison, the GAGE and the CMDL time series were first compared at the common site of Samoa. On the basis of a linear fit to the monthly mean ratios of CMDL/GAGE over the time period from 1987 to 1993 the CMDL measurements are on average 2.3 ± 0.4% (standard error) higher for CCl3F and −0.4 ± 0.6% higher for CC12F2 with no significant drift between the two time series for CCl3F but with a CC12F2 drift for CMDL/GAGE of 0.3 ± 0.2%/yr. These differences are consistent with the results of laboratory intercomparisons performed at approximately the end of this period: 2.6% and 0.6% higher CMDL values for CCl3F and CC12F2, respectively (F.J.F. and J. Elkins, private communication, 1996). The consistency with the laboratory results is similar if global means from the two networks are compared (2.7% and 0.6% higher CMDL values in 1992/1993). Table 1 indicates that the northernmost semihemisphere representativeness of Barrow alone might have

Table 1. Annual Mean Concentrations (ppt) of CCl3F Calculated Using the CCM2 for 1987 for a Global Release Rate of 345 × 10^6 kg/yr and for Two Different Spatial Distribution of Release (see Figure 4)

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<tr>
<td>Emissions (MMF)</td>
<td>Emissions (HP)</td>
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<tr>
<td>90°–30°N</td>
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<td>247.52</td>
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<td>30°–90°S</td>
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<td>225.38</td>
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<tr>
<td>Global mean</td>
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<td>234.87</td>
<td>0.10</td>
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Individual Sites

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<tr>
<td>Barrow, Alaska</td>
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<tr>
<td>Mace Head, Ireland</td>
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<tr>
<td>Cape Meares, Oregon</td>
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<td>247.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Niwot Ridge, Colorado</td>
<td>247.6</td>
<td>248.8</td>
<td>-1.1</td>
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<tr>
<td>Ragged Pt., Barbados</td>
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<td>241.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Cape Matatula, Samoa</td>
<td>228.6</td>
<td>228.8</td>
<td>-0.2</td>
</tr>
<tr>
<td>Cape Grim, Tasmania</td>
<td>225.2</td>
<td>225.5</td>
<td>-0.3</td>
</tr>
<tr>
<td>Global mean (CMDL sites)</td>
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<td>235.3</td>
<td>-0.1</td>
</tr>
<tr>
<td>Global mean (GAGE sites)</td>
<td>236.2</td>
<td>236.0</td>
<td>0.2</td>
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Results are given first for semihemispheric boxes extending from 1000 to 500 mbar and then for individual locations of the AGA and CMDL sampling networks. Pollution has been removed from the individual site values but not from the CCM2 semihemispheric means.

Table 1 also shows the calculations at locations in the northernmost semihemisphere (Barrow, Alaska, 71°N, 157°W and Niwot Ridge, Colorado, 40°N, 105°W) where flask samples have been collected routinely since 1977 by the Climate Monitoring and Diagnostics Laboratory (CMDL) of the National Oceanic and Atmospheric Administration (NOAA) [Elkins et al., 1993]. Comparisons of the AGA measurements against the publicly available flask sample time series from 1987 to 1993 provide a second test and some support for the representativeness of Mace Head. To establish a basis of comparison, the GAGE and the CMDL time series were first compared at the common site of Samoa. On the basis of a linear fit to the monthly mean ratios of CMDL/GAGE over the time period from 1987 to 1993 the CMDL measurements are on average 2.3 ± 0.4% (standard error) higher for CCl3F and −0.4 ± 0.6% higher for CC12F2 with no significant drift between the two time series for CCl3F but with a CC12F2 drift for CMDL/GAGE of 0.3 ± 0.2%/yr. These differences are consistent with the results of laboratory intercomparisons performed at approximately the end of this period: 2.6% and 0.6% higher CMDL values for CCl3F and CC12F2, respectively (F.J.F. and J. Elkins, private communication, 1996). The consistency with the laboratory results is similar if global means from the two networks are compared (2.7% and 0.6% higher CMDL values in 1992/1993). Table 1 indicates that the northernmost semihemisphere representativeness of Barrow alone might have

Figure 4. Percentage of global emissions of CCl3F in 1987 from several continental regions and within each semihemisphere of the globe based on the emission scenarios of Hartley and Prinn [1993] and McCulloch et al. [1994] [from Hartley et al., 1996].
The similarity shown in Figure 5 between the observed decline in the latitudinal gradient and that calculated using the AGA release estimates indicates that recent reductions in these release rates have produced changes in the northernmost/southernmost semihemisphere differences which are consistent with the measured Mace Head/Cape Grim differences (see also Plate 1). This consistency is also seen in Figure 2 where after 1986 the green asterisks fit the green line best (the Ireland/Oregon results, which include Oregon values only up to June 1989) and the black asterisks fit the black line best (the Tasmania results). Therefore there is no evidence that the Mace Head measurements are any less typical of the northernmost semihemisphere box model value than they were in the past, and the uncertainty in this statement is approximately 1 ppt (or 0.5%). The uncertainty that this introduces into the AGA-derived emission estimates is small (roughly $5 \times 10^6$ kg) relative to the error bars shown in Figure 1. It may also be noted that the Mace Head/Cape Grim differences in Figure 5 are clearly more consistent with the AGA emission estimates for 1993 and 1994 than with the reporting company values (combined with an assumption of constancy in nonreporting company releases).

5. Trends in Total Anthropogenic Atmospheric Chlorine

The GAGE/AGAGE program provides measurements of CH$_3$CCl$_3$, CCIF, and CCl$_4$/FCCIF$_2$ in addition to CCl$_3$F and CCl$_2$F$_2$. Since the only other significant anthropogenic source of chlorine is CHFCl$_2$ (HCFC-22), summing the GAGE-measured chlorine values provides a good estimate of the trends in atmospheric anthropogenic chlorine. The measurements of CH$_3$CCl, and CCl$_3$/FCCIF$_2$ have recently been reported by Prinn et al. [1995] and Fraser et al. [1996]. A paper is in preparation updating the CCl$_4$ measurements beyond 1985. The data on all species (except CHFCl$_2$) through June 1994 are available from the Carbon Dioxide Information Analysis Center (CDIAC) at the U.S. Department of Energy, Oak Ridge National Laboratory, through Internet (cdp@ornl.gov).

ALE/GAGE measurements of CCl$_4$ through 1985 were reported by Simmonds et al. [1988]. Recently, new absolute calibration standards for CCl$_4$ have been prepared at SIO by procedures similar to those described in obtaining chlorofluorocarbon and CH$_3$CCl$_3$ standards [Prinn et al., 1995]. Based on analyses of five secondary calibration gases, the preliminary value of the factor to be applied to the original ALE gases is 0.629. The observations used here are reported on this scale. This change of scale was anticipated by Simmonds et al. [1988]; it is now within 5% of scales used by Yokohata et al. [1985] and by CMDL. The CCl$_4$ time series indicates that atmospheric concentrations maximized in 1990 and have decreased since that time (P. G. Simmonds et al., manuscript in preparation, 1996).

The chlorine loading can be defined as the mixing ratio of chlorine in long-lived anthropogenic chlorocarbons in the troposphere. The mean tropospheric mixing ratios of the AGA gases is estimated by combining the average AGA-measured values for the lower troposphere with results from a two-dimensional model which has been optimized to fit the measurements and which provides estimates of the concentrations in the upper troposphere. This model yields tropospheric averages which are equal to approximately 99% of the mean of the four semihemispherically located values. Figure 6 shows...
the time series of the contributions of these gases to chlorine loading since 1978. It shows that most of the time it is not possible to obtain a global average chlorine loading directly from the measurements (e.g., the GAGE CCl₃F/CFC₁₂F₃ measurements did not begin at the fourth site until 1985). However, by using the optimally fit model and archived air measurements of CCl₃F/CFC₁₂F₃ from Cape Grim [Fraser et al., 1996], a complete time series can be obtained which overlaps the GAGE measurements where and when they are available. Figure 6 shows that the chlorine loading resulting from the five AGA-measured species maximized in 1992 at 2.85 ppb, primarily because of the large drop in the 1993 CH₃CCL₄ emissions.

Atmospheric concentrations of CHClF₂ have been measured in air samples archived at Cape Grim since 1978. These measurements have been fitted to two-dimensional model calculations, which used emissions derived from production data [SAFEAS, 1996] to provide an estimated atmospheric lifetime for CHClF₂. The two-dimensional model then provides a simulation of the temporal evolution of the global distribution of CHClF₂. The procedure is similar to that described by Fraser et al. [1996]. The AGAGE calibration for CHClF₂ is almost identical (closer than 1%) with that of CMDL. The CHClF₂ results will be presented in a separate publication, but if the CHClF₂ emissions are included in the chlorine loading, a maximum in chlorine loading due to the six components with strongly varying emissions also occurred at the end of 1992 of 2.95 ± 0.04 ppb. The (systematic) uncertainty in this estimate arises in approximately equal parts from how well the measurements can be extrapolated to a tropospheric content using the two-dimensional model (assumed to be 1%; note that Table 1 shows only a 0.5% difference between the CCM2 and the measurement mean for the lower troposphere) and from absolute and transfer calibration uncertainties (1.3% for CCl₃F and 0.9% for CCl₂F₂, CBr₄; 2% for CCl₂FCCCl₂F, Fraser et al. [1996]; and conservatively, 5% from the SIO 1993-based calibrations of CH₃CCl₃, CCl₄, and CHClF₂).

By early 1995 the anthropogenic chlorine loading due to these six compounds has decreased by 0.02 ± 0.01 ppb since 1992. The uncertainty in this estimate is due to the random year-to-year uncertainties which result from measurement and modeling errors; this figure is based on the imprecise fit of the two-dimensional model (which has been optimally adjusted as described in section 2) to the annual means of the measurements at each site. Since other minor sources of anthropogenic chlorine such as CFC-114 (CCl₃F/CFC₁₂F₃), HCFC-141b (CH₃CFC₁₂), and HCFC-142b (CH₃CCF₂), which are beyond the scope of this paper to discuss, may have contributed an increase of 0.1-0.02 ppb between 1992 and early 1995 [e.g., Montzka et al., 1994, 1996; Sanhueza et al., 1995; Onum et al., 1995], it is only possible to conclude at this time that total anthropogenic chlorine in the troposphere is unlikely to have increased since 1992.

Figure 6 also shows the IS92 emission scenarios for these compounds [Prather et al., 1996]. The measurements and the IS92 figures began to diverge in 1990 and the measurements show that the maximum occurred three years earlier and with a value 0.2 ppb (7%) less than projected under the (unadjusted) IS92 scenario. This overprediction for IS92 was previously pointed out by Fraser et al. [1995]. Approximately 0.1 ppb of the difference in chlorine loading results from the new AGA calibration of CCl₄; the IS92 scenario used the ALE/GAGE CCl₄ calibration scale reported by Simmonds et al. [1983].

After this manuscript was submitted, calculations of chlorine loading based on the CMDL measurements were published [Montzka et al., 1996]. Their chlorine loading associated with the six gases discussed in the paper is approximately 70 ppt larger in mid-1995 than we are reporting. This is because almost all their calibrations are slightly higher than those in the SIO 1993 scale, with the largest difference being approximately 5% for CH₃CCL₄, CH₃CFC₁₂, and CH₃CCF₂. Moreover, they report a maximum which occurs later by at least a half a year than ours. This may be primarily because their global mean for CCl₃F₂ for mid-1995 is approximately 9 ppt (1.6%) larger than the AGA value. Thus appears to have been a continuation and, perhaps, an acceleration of the drift in the differences in CCl₃F₂ between the two networks referred to earlier in section 4. This difference is significant because we are very confident in the continuity and propagation of the GAGE/AGAGE calibration since 1990.
mates obtained from production figures (as we have reported previously). Global production-derived estimates have been about 10% larger for CC12F 2 prior to 1989 than global estimates. It is estimated that the emissions from nonreporting companies have been reduced releases from recent production or that there has been a very rapid decrease in production by the nonreporting companies. In 1993 and 1994 the AGA emission estimates are significantly less than the global production-derived estimates; possible explanations are that there has been a very rapid decrease in production by the nonreporting companies. It is estimated that the emissions in 1993 and 1994 averaged 255 and 125 x 10^6 kg annually for CC12F 2 and CC13F, respectively, or approximately 55 and 35% of the 1986 emissions.

The AGA estimates of the lifetimes are a little longer than those in our previous publication [Cunnold et al., 1994] because a transfer time of 2 years between the troposphere and the stratosphere has now been adopted on the basis of other model results. The lifetime estimates are 52 ± 23 years for CC13F and 172 ± 416 years for CC12F 2. The lifetime discrepancy for CC12F 2 (versus the models) and the corresponding overall emission discrepancy suggests a shorter residence time than 4 years in nonhermetically sealed uses and an increase in production prior to 1989 by nonreporting companies.

Simmonds et al. [1996] have sorted Mace Head observations according to trajectory directions and have inferred mean emissions of the GAGE-measured gases from Europe. Their results indicate that the European emissions of CC13F and CC12F 2 have decreased roughly twice as fast, since 1987, as industry figures have indicated. An independent analysis of Mace Head pollution events in the current manuscript results in similar conclusions.


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