CHAPTER 1

Source Gases: Concentrations, Emissions, and Trends

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Chapter 1
Source Gases: Concentrations, Emissions, and Trends

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The major anthropogenic source gases implicated directly in halogen induced stratospheric ozone loss, *i.e.*, chlorofluorocarbons (CFCs), hydrochlorofluorocarbon-22 (HCFC-22), the halons, methyl chloroform and carbon tetrachloride, continue to grow in concentration in the background troposphere of both hemispheres. Total tropospheric chlorine is increasing by ≈0.1 parts per billion by volume (ppbv) per year. CFCs contribute approximately 75 percent to this increase, methyl chloroform 13 percent, and HCFC-22 ≈5 percent.

The 1989 global mean concentrations and trends of the various source gases that can directly or indirectly influence the global abundance of stratospheric and tropospheric ozone are given in Table 1-1. In general, the data are similar to those reported for 1987 in the previous assessment (WMO, 1990b), but there have also been some important new developments.

CFC-11 and CFC-12 trends have not changed significantly since the last assessment. The global CFC-113 trend in 1989 (=5–6 parts per trillion by volume (pptv), 9 percent) is higher than observed in 1987 (=4–5 pptv, 7 percent). Absolute calibration remains uncertain (±10 percent). The global average CCl₄ concentration for 1989 (=107 pptv) is lower than that reported for 1987 in the last assessment (=140 pptv), due essentially to a change in calibration based on a comparison of Atmospheric Lifetime Experiment–Global Atmospheric Gases Experiment (ALE-GAGE) data with data collected in several other programs. Absolute calibration remains uncertain (±10 percent).

The CH₃CCl₃ global trend in 1989 from the ALE-GAGE program (5.5 pptv, 3.7 percent) is lower than that reported for 1987 (6.0 pptv, 4.0 percent). Absolute calibration remains uncertain (±10 percent), and the ALE-GAGE calibration could be high by =15 percent, inferring a global mean 1989 concentration of 135 pptv rather than 150 pptv based on the current ALE-GAGE calibration scale. The oceans are a significant sink for CH₃CCl₃, implying that computed OH levels are 5–10 percent too high if this sink is ignored. These variations are well within the uncertainty of the rate of methyl chloroform-hydroxyl radical reaction (±40 percent). By analogy, HCFCs and HFCs may also have an oceanic sink although HCFCs and HFCs are more resistant to hydrolysis than CH₃CCl₃. Assuming that the ALE-GAGE calibration and industrial emissions are accurate, then the CH₃CCl₃ trend implies that the CH₃CCl₃ sink and hence global OH levels are increasing by 1.0±0.8 percent per year.

Spectroscopic and gas chromatographic measurements of HCFC-22 both show similar global increases of 6–7 pptv per year. The calibration uncertainty is ±10 percent.

Exponential increases in the bromine containing chemicals Halon-1211 and -1301 have been observed (=15 percent and =20 percent per year respectively), although absolute calibration remains quite uncertain (±15 and ±40 percent respectively). Methyl bromide is the major source of stratospheric bromine. While the possibility of a trend in methyl bromide cannot be assessed due to lack of data, a large anthropogenic methyl bromide source has been previously suggested.

Nitrous oxide continues to increase globally about 0.8 ppbv per year. New global nitrous oxide sources have been proposed (adipic acid production, legume pastures), but the sum of all known sources is not sufficient to balance the calculated atmospheric sink.

The rate of increase of global tropospheric CH₄ continues to decline, with increases of 17–21 ppbv per year observed during 1978–1982 and 12–14 ppbv per year during 1988–1990, or even lower in the Southern Hemisphere. No satisfactory explanation of this phenomenon has been put forward. Ice core studies indicate that CH₄ growth rates have shown significant temporal variability over the past 100 years. The problem of reconciling atmospheric CH₄ observations with estimates of emission sources is severely limited by the lack of
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observations in major source regions. There is significant uncertainty in the direct estimates of CH₄ emissions from rice agriculture. Indian studies suggest that the global CH₄ source from rice agriculture may be significantly lower than 100 Tg per year. Recent methane isotopic studies suggest that approximately 20 percent of the total methane source (500 Tg [10¹² g] per year) is fossil, and 10 percent is from biomass burning. The CH₄ sink due to OH oxidation may be increasing due to increasing levels of OH radical. Global levels of H₂ are increasing (0.5–0.7 percent per year), presumably partly in response to growing CH₄ levels.

Increasing CO concentrations of about 1 ppbv per year appear to be confined to the Northern Hemisphere. In the Southern Hemisphere there have been periods of CO growth (1986–1988) and decline (1983–1985), with no overall change from 1978 to 1990. Some CO sources are known to be increasing (CH₄) and others decreasing (fuel CO emissions from OECD* countries). The CO sink due to OH oxidation may also be increasing due to increasing levels of OH radical.

* Organization for Economic Cooperation and Development (OECD) countries include Australia, Austria, Belgium, Canada, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Japan, Luxembourg, Netherlands, New Zealand, Norway, Portugal, Spain, Sweden, Switzerland, Turkey, U.K., U.S., and Yugoslavia (Special Member).
1.1 INTRODUCTION

Source gases are defined as those gases that influence levels of stratospheric ozone (O3) by transporting species containing halogen, hydrogen, and nitrogen to the stratosphere that are important in O3 destruction. Examples are the CFCs, methane (CH4), and nitrous oxide (N2O). Other source gases that also come under consideration in an atmospheric O3 context are those that are involved in the O3 or hydroxyl (OH) radical chemistry of the troposphere. Examples are CH4, carbon monoxide (CO) and nonmethane hydrocarbons (NMHCs). Most of the source gases, along with carbon dioxide (CO2) and water vapor (H2O), are climatically significant and thus affect stratospheric O3 levels by their influence on stratospheric temperatures. Carbonyl sulphide (COS) could affect stratospheric O3 through maintenance of the stratospheric sulphate aerosol layer, which may be involved in heterogeneous chlorine-catalyzed O3 destruction.

This chapter updates the previous reviews of trends and emissions of source gases, either from the context of their influence on atmospheric O3 (WMO, 1986; 1990a, b) or global climate change (IPCC, 1990). The current (1989) global abundances and concentration trends of the trace gases are given in Table 1-1.

1.2 CFCs AND CARBON TETRACHLORIDE: GLOBAL DISTRIBUTIONS, TRENDS AND CALIBRATION

The CFCs (-11, -12, and -113) and carbon tetrachloride (CCl4) compose 70 percent of the anthropogenic organochlorine loading of the troposphere (CFC-12, 28 percent; CFC-11, 23 percent; CCl4, 13 percent; CFC-113, 6 percent). They are inert in the troposphere but photodissociate in the stratosphere and hence are a major source of stratospheric reactive chlorine. The CFCs are used as refrigerants, foam blowing agents and solvents. CCl4 is used in the production of CFCs.

1.2.1 CFC-11 and CFC-12

There are several long term measurement programs for CFC-12 and CFC-11. National Oceanic and Atmospheric Administration–Climate Monitoring and Diagnostics Laboratory (NOAA–CMDL) have run a global program since 1977 based on weekly flask measurements at Barrow, AK; Niwot Ridge, CO; Mauna Loa, HI; Cape Matatula, Samoa; and the South Pole. The 1989 global mean concentrations for CFC-12 and CFC-11 were 452 and 268 pptv respectively (mean of hemispheric means; Northern Hemisphere: Barrow, Niwot Ridge and Mauna Loa; Southern Hemisphere, Samoa), increasing at 16.9±0.2 and 10.1±0.1 pptv per year, or 3.7 percent and 3.8 percent per year respectively in 1989, based on linear regressions. The data are reported in the original Oregon Graduate Institute for Science and Technology (OGIST) scale and are shown in Figures 1-1 and 1-2 (Thompson et al., 1990). A possible CFC-12 calibration problem has been identified in the NOAA–CMDL data (J. Elkins, NOAA–CMDL, personal communication). A recent reevaluation of the flask data indicates that the long-term, linear, global growth of CFC-12 was 16.1±0.3 pptv per year, based on data from 1977 to 1991. NOAA–CMDL in situ measurements (12 per day) of CFC-12 and CFC-11 commenced at Barrow, Mauna Loa, and Samoa (1986) and at the South Pole (1987) (Thompson et al., 1990; Hall et al., 1990); preliminary CFC-12 data have been reported in the recently prepared NOAA–CMDL gravimetric scale. The 1989 global mean CFC-12 concentration was 462 pptv, increasing at about 20 pptv per year, or 4.4 percent per year in 1989. The differences between the global mean derived from flask and in situ measurements presumably reflect differences between the OGIST and NOAA–CMDL CFC-12 calibration scales.

In situ measurements (4–12 per day) of CFC-12 and CFC-11 have been made in Ireland, Oregon, Barbados, Samoa, and Tasmania since 1978 as part of the ALE–GAGE program (Cunnold et al., 1986). The 1989 global mean concentrations for CFC-12 and CFC-11 were 453 and 255 pptv respectively (mean of hemispheric means; Northern Hemisphere: Ireland, Barbados; Southern Hemisphere, Tasmania), increasing at 18.2±0.3 and 9.3±0.1 pptv per year, or 4.0 percent and 3.7 percent per year in 1989, based on linear regressions (Cunnold et al., 1986; Prinn et al., 1991b). The data are in the GAGE scale (CFC-11, GAGE scale = OGIST scale x 0.96; CFC-12, GAGE scale = OGIST scale x 0.95) and are also shown in Figures 1-1 and 1-2. The long term stability of the OGIST CFC-11 scale has been possibly but not abso-
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### Table 1-1 Updated global trends and tropospheric concentrations of source gases for 1989. Adapted from WMO (1990b).

<table>
<thead>
<tr>
<th>Source gas</th>
<th>Concentration 1989 (pptv)</th>
<th>Increase 1989 pptv/year</th>
<th>percent/year</th>
<th>Calibration uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>1689x10³</td>
<td>(12–14)x10³</td>
<td>0.7–0.8</td>
<td>±1%</td>
</tr>
<tr>
<td>H₂</td>
<td>515x10³</td>
<td>(2.7–3.7)x10³</td>
<td>0.5–0.7</td>
<td>?</td>
</tr>
<tr>
<td>N₂O</td>
<td>(307–308)x10³</td>
<td>(0.6–0.9)x10³</td>
<td>0.2–0.3</td>
<td>±1%</td>
</tr>
<tr>
<td>CO NH</td>
<td>(100–150)x10³</td>
<td>(0.4–1.2)x10³</td>
<td>0.3–1.0</td>
<td>±5%</td>
</tr>
<tr>
<td>SH</td>
<td>(50–60)x10³</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>352.2x10⁶</td>
<td>1.6x10⁶</td>
<td>0.5</td>
<td>&lt;0.1%</td>
</tr>
<tr>
<td>C₂H₆ NH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCl₂F₂</td>
<td>453</td>
<td>16.9–18.2*</td>
<td>3.7–4.0</td>
<td>±2%</td>
</tr>
<tr>
<td>CCl₃F</td>
<td>255–268</td>
<td>9.3–10.1</td>
<td>3.7–3.8</td>
<td>±1%</td>
</tr>
<tr>
<td>CCl₃FCCIF₂</td>
<td>64</td>
<td>5.4–6.2</td>
<td>9.1</td>
<td>±10%</td>
</tr>
<tr>
<td>CCl₂F₂CCIF₂</td>
<td>15–20</td>
<td>=1</td>
<td>=6</td>
<td></td>
</tr>
<tr>
<td>CCl₃F₅F₃</td>
<td>=5</td>
<td>=0.3</td>
<td>=6</td>
<td></td>
</tr>
<tr>
<td>CCl₃</td>
<td>107</td>
<td>1.0–1.5</td>
<td>1.2</td>
<td>±10%</td>
</tr>
<tr>
<td>CH₂Cl₃</td>
<td>135</td>
<td>4.8–5.1</td>
<td>3.7</td>
<td>±15%</td>
</tr>
<tr>
<td>CHClF₂</td>
<td>110</td>
<td>5–6</td>
<td>6–7</td>
<td>±10%</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>600</td>
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<td></td>
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<tr>
<td>CHCl₁</td>
<td>≈10</td>
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<td></td>
<td></td>
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<tr>
<td>CH₂Cl₂</td>
<td>≈35</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CCl₂CCl₂</td>
<td>≈30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₂ClCH₂Cl</td>
<td>≈35</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CHClCCl₂</td>
<td>≈10</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CH₃Br</td>
<td>10–15</td>
<td>?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₂Br₂</td>
<td>2–3</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>CHBrCl₂</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₄Br₂</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₅Br</td>
<td>2–3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBrClF₂</td>
<td>1.6–2.5</td>
<td>0.2–0.4</td>
<td>15</td>
<td>±15%</td>
</tr>
<tr>
<td>CBrF₃</td>
<td>1.8–3.5</td>
<td>0.4–0.7</td>
<td>20</td>
<td>±40%</td>
</tr>
<tr>
<td>COS</td>
<td>≈500</td>
<td>?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Cl</td>
<td>3800</td>
<td>110</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Percent anthropogenic</td>
<td>≈80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Br</td>
<td>40</td>
<td>0.9</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Percent anthropogenic</td>
<td>≈12 (halons only)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Data subject to revision; significantly lower trends may result (see text).*
Figure 1-1 CFC-12 observations (pptv) in the four semihemispheres (NOAA: Thompson et al., 1990; GAGE: Cunnold et al., 1986; Prinn et al., 1991b; UT: Makide et al., 1987; Makide 1991). Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: NOAA, J. Elkins; GAGE, R. Prinn; UT, Y. Makide; UEA, S. Penkett; SIO, R. Weiss.
Figure 1-2 CFC-11 observations (pptv) in the four semihemispheres (NOAA: Thompson et al., 1990; GAGE: Cunnold et al., 1986; Prinn et al., 1991b; UT: Makide et al., 1987; Makide 1991) some of the data are unpublished and subject to revision. Data should not be used for further analysis without consulting the principal investigators: NOAA, J. Elkins; GAGE, R. Prinn; UT, Y. Makide; UEA, S. Penkett; SIO, R. Weiss; FIAER, H. Scheel.
lutely demonstrated by extensive, periodic internal comparisons of several original ALE-GAGE calibration gases and by a comparison of measurements made in 1978–1979 in the ALE-GAGE program in Tasmania with modern measurements on air archived from that period. These experiments limit the magnitude of a calibration drift component of the observed trend to about 0.1 percent per year. A possible CFC-12 calibration problem has been identified in the GAGE data, which are currently being reevaluated. Lower trends will probably result (D. Cunnold, GAGE-GIT, personal communication) although the changes are likely to be small.

The global CFC-11 ratio (GAGE (in situ) NOAA–CMDL (flask) = 0.95) reflects the difference between the two calibration scales involved (GAGE/OGIST = 0.96), whereas the global CFC-12 ratio (GAGE (in situ)/NOAA–CMDL (flask) = 1.00) does not (GAGE/OGIST = 0.95). This requires further investigation. The 1989 mean CFC-12 and CFC-11 concentrations at Tasmania (41°S) were 441 and 247 pptv, which, when compared to the South Pole observations above, suggest that the NOAA–CMDL and GAGE scales agree to within 2 percent (CFC-12) and 1 percent or better (CFC-11).

In situ CFC-11 measurements (24 per day) have been made at Cape Point, South Africa, since 1980 (Scheel et al., 1990; Brunke and Scheel, 1991). The 1989 mean CFC-11 concentration at Cape Point (34°S) was 256 pptv, increasing at 9.3±0.1 pptv per year or 3.6 percent per year in 1989 based on a linear regression. The data are reported in the original OGIST scale and are also shown in Figure 1-2. The 1989 mean CFC-11 concentration and trend in Tasmania (41°S), 247 pptv, is in agreement with the Cape Point data and shows that the South Pole observations agree with the GAGE program data, which are shown in Figure 1-2. The 1989 mean CFC-11 concentration at Cape Point (34°S) was 256 pptv, increasing at 9.3±0.1 pptv per year.

Flask measurements of CFC-12 and CFC-11 (1 week every 6 months) have been made on Hokkaido, Japan (40°45′N), since 1979 (Makide et al., 1987; Makide, 1991) and at Syowa Station, Antarctica (69°S), several times per year since 1982 (Makide 1991). On Hokkaido CFC-11 and CFC-12 increases of 18.6±0.2 and 9.4±0.2 pptv per year respectively have been observed, based on linear regressions. The 1989 mean CFC-12 and CFC-11 concentrations at Hokkaido are 481 and 259 pptv respectively and at Syowa 441 and 235 pptv respectively. The data are reported in independently prepared University of Tokyo (UT) calibration scales and are shown in Figures 1-1 and 1-2. A direct interlaboratory comparison of the GAGE and UT CFC-12 and CFC-11 calibration scales and a comparison of CFC-12 and CFC-11 data collected at Hokkaido (UT), Ireland (GAGE), Syowa (UT), and Tasmania (GAGE) has shown that GAGE data agree to within 2 percent for CFC-12 (GAGE lower) and within 3 percent for CFC-11 (GAGE higher) (Y. Makide and P. Fraser, unpublished data).

Measurements of CFC-12 and CFC-11 have been made in the free troposphere via aircraft over Europe and the North Atlantic Ocean since 1976 (Scheel et al., 1988; Seiler and Scheel, 1991). CFC-12 and CFC-11 increases of 16.3±0.5 and 10.6±0.3 pptv per year have been measured over the period 1976–1987, similar to the trends observed from ground-based observations in the Northern Hemisphere. These aircraft data are based on a commercially available Scott-Marrin standard.

Free tropospheric measurements of CFC-12 and CFC-11 have been made via aircraft over Japan (33°–38°N) since 1978 (Hirot a et al., 1988; Hirot a and Sasaki, 1991). CFC-12 and CFC-11 increases of 16.2±0.7 and 10.3±0.4 pptv per year have been measured over the period 1978–1990, similar to the trends observed over Europe. These aircraft data are based on a commercially available Seitetsu Kagaku and Nihon Sanso standards, whose absolute concentration is certified to ±5 percent.

A comparison of shipboard measurements of CFC-12 and CFC-11 from 1981 to 1984 on the North and South Atlantic (Penkett, 1991a) to GAGE data from corresponding latitudes shows that the GAGE and Penkett data agree to within 3 percent for CFC-12 (GAGE higher) and to within 1 percent for CFC-11 (GAGE higher). Similarly, a comparison of shipboard measurements of CFC-12 and CFC-11 from 1983 to 1990 on the North and South Atlantic (Weiss, 1991) to GAGE data from corresponding latitudes shows that the GAGE and Weiss data agree to within 2 percent for CFC-12 (GAGE lower) and to within 2 percent for CFC-11 (GAGE higher).

1.2.2 CFC-113

Flask measurements of CFC-113 have been made on Hokkaido, Japan (40°45′N) since 1980 and at

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Syowa Station (69°S) (10 days each winter) since 1987 (Makide et al., 1987; Makide, 1991). On Hokkaido the mean CFC-113 increase over the period 1979–1990 was 5.5±0.2 pptv per year and 7.9±0.3 pptv over the period 1987–1990, based on linear regressions. The data are reported in an independently prepared UT calibration scale and are shown in Figure 1-3.

Real-time measurements (12 per day) of CFC-113 have been made in Ireland, Oregon, Barbados, Samoa, and Tasmania since 1982 as part of the GAGE program (Fraser et al., 1991). The 1989 global mean CFC-113 concentration was 64 pptv (mean of hemispheric means; Northern Hemisphere: Ireland, Barbados; Southern Hemisphere, Tasmania), increasing at 5.8±0.4 pptv per year, or 9.1 percent per year in 1989, based on linear regressions (Fraser et al., 1991). The GAGE CFC-113 data (Figure 1-3) are obtained relative to OGIST calibration gases, but are reported in the GAGE scale, which is based on an interlaboratory comparison to the UT CFC-113 scale (Makide et al., 1987). This comparison showed that the UT/OGIST ratio is 1.4-1.5 (Y. Makide and P. Fraser, unpublished data).

In situ measurements of CFC-113 at Cape Point, South Africa (Brunke and Scheel, 1991) show a lower growth for CFC-113 (2.4±0.2 pptv per year; 7.3 percent per year in 1989). The data are reported in the OGIST scale, so the increase would translate to ~3.5 pptv per year in the UT scale. Measurements of CFC-113 in the free troposphere over Europe and the North Atlantic during the period 1982–1987 show an increase of 6.6±0.3 pptv per year (Seiler and Scheel, 1991). The data are based on a Scott–Marrin calibration standard, which gives CFC-113 concentrations that are a factor of ~2 higher than data obtained using OGIST calibration.

NOAA–CMDL have produced a new gravimetric CGC-113 scale, which is about 40 percent higher than the OGIST scale (NOAA–CMDL/OGIST = 1.37) (Thompson et al., 1990) and therefore presumably about 3–5 percent lower than the UT (=GAGE) scale. Measurements of CFC-113 at Cape Grim, Tasmania (41°S), have been compared to CFC-113 measurements on the South Atlantic at similar latitudes and times, which were obtained using an independent calibration scale University of East Anglia (UEA) (Penkett, 1991). The Atlantic data were approximately 10–20 percent lower, which probably reflects the difference in calibration scales (i.e., GAGE/UEA =1.1–1.2; thus UEA/OGIST =1.2–1.4).

It would appear that three independent laboratories (UT, NOAA–CMDL and UEA agree to within ±10 percent on CFC-113 calibration.

1.2.3 CFC-114 and CFC-114a

Rasmussen et al., (1990) has reported growth rates for CFC-114 (CClF$_3$CClF$_3$) and CFC-114a (CCl$_2$FCF$_3$) from the OGIST global flask sampling network from 1979 to 1990 of approximately 6 percent per year. Absolute concentrations were not reported. There have been no new data reported for CFC-115.

1.2.4 Carbon Tetrachloride

In situ CCl$_4$ measurements have been made at the GAGE stations since 1978 (Simmonds et al., 1988). The data (Figure 1-4) show a global mean 1989 concentration of 134 pptv, based on data from Ireland, Barbados, and Tasmania, and an increase over the entire record of 1.6±0.3 pptv per year, or 1.2 percent per year in 1989.

A similar CCl$_4$ increase has been observed from in situ measurements at Cape Point (1.7±0.1 pptv per year) over the period 1980–1990 (Figure 1-4). This program employs the same calibration scale as the GAGE program. The 1989 mean concentration (128 pptv) at Cape Point (32°S) is very similar to that observed (130 pptv) at Cape Grim, Tasmania (41°S). However in situ measurements in 1989 at Samoa (14°S) and the South Pole using the new NOAA–CMDL gravimetric calibration scale gave mean concentrations of 104 and 106 pptv respectively (Thompson et al., 1990; Hall et al., 1990), whereas GAGE measurements at Samoa in 1989 average about 132 pptv, suggesting that concentrations in the NOAA–CMDL scale are ~20 percent lower than those in the GAGE scale.

Flask measurements of CCl$_4$ on Hokkaido, (40°–45°N) over the period 1979–1990 show an increase of 1.4±0.2 pptv per year (Makide et al., 1987; Makide, 1991). A direct interlaboratory comparison between GAGE and Makide indicate that the GAGE CCl$_4$ scale is ~20 percent higher than Makide (Y. Makide and P. Fraser, unpublished data).

Measurements of CCl$_4$ in the free troposphere over Europe and the North Atlantic during the period
Figure 1-3 CFC-113 observations (pptv) in the four semihemispheres (GAGE: Fraser et al., 1991; Prinn et al., 1991b; UT: Makide, 1991). Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: GAGE, R. Prinn; UT, Y. Makide; UEA, S. Penkett.
Figure 1-4 Carbon tetrachloride (pptv) in the four semihemispheres. (GAGE: Simmonds et al., 1988; Prinn et al., 1991b; UT: Makide et al., 1987; Makide, 1991; CSIR-FIAER: Scheel et al., 1990). Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: GAGE, R. Prinn; UT, Y. Makide; UEA, S. Penkett; FIAER, H. Scheel
1976–1987 show an increase of 2.0±0.3 pptv per year (Seiler and Scheel, 1991). These data are based on a Scott-Marrin calibration standard, which gives CCl4 concentrations that are a factor of ≈1.15 lower than those based on the GAGE calibration.

Measurements of CCl4 at Cape Grim (41°S) have been compared to CCl4 measurements on the South Atlantic at similar latitudes and times, which were obtained using an independent calibration scale (UEA) (Penkett, 1991a). The Atlantic data were approximately 15 percent lower, which probably reflects the difference in calibration scales (i.e., GAGE/UEA =1.15). A direct comparison of National Institute of Standards and Technology (NIST) and GAGE CCl4 standards indicates that the GAGE/NIST ratio is ≈1.35 (Fraser, personal communication, 1991).

It would appear that five independent laboratories (UT, NOAA-CMDL, UEA, Fraunhofer Institute for Atmospheric Environmental Research (FIAER) (Scott-Marrin), and NIST) agree to within ±10 percent on CCl4 calibration, and are ≈20 percent lower than GAGE.

1.3 METHYL CHLOROFORM AND HCFC-22

Methyl chloroform (CH3CCI3) and HCFC-22 (CHCIF2) are important trace gases in the global atmosphere. They constitute about 17 percent of the tropospheric anthropogenic organochlorine loading (CH3CCI3, 14 percent; CHCIF2, 3 percent) and both are partially removed from the atmosphere by reaction with OH. Assuming emissions and absolute abundances of these species are known, they can be used to calculate average tropospheric OH levels (for CH3CCI3, see Prinn et al., 1987, 1992). Methyl chloroform is used as an industrial solvent and HCFC-22 is being increasingly used as a substitute for CFCs.

1.3.1 Global distributions and trends

Long-term, high-frequency measurements (4-12 per day) of CH3CCI3 have been made in Ireland, Oregon, Barbados, Samoa and Tasmania (Prinn et al., 1987, 1991a) since 1978 as part of the ALE-GAGE program and on Hokkaido twice a year (10 days every 6 months) since 1979 and at Syowa Station in Antarctica (several times per year) (Makide et al., 1987; Makide, 1991). January measurements made in the Pacific North West (PNW) of the United States and at the South Pole since 1975 have been published (Rasmussen and Khalil, 1986; Khalil and Rasmussen, 1990b). Mid-tropospheric CH3CCI3 data have been obtained by aircraft air sampling over Europe and the North Atlantic by FIAER since 1978 (Scheel et al., 1988).

The available data are shown in Figure 1-5. Twelve years of ALE-GAGE CH3CCI3 data (July 1978 to June 1990) have recently been analyzed (Prinn et al., 1992) showing a global trend of 5.5±0.2 pptv per year or 4.4±0.2 percent per year (mid-1984). The 1989 global mean concentration was 150.0 pptv (based on data from Ireland, Barbados, and Tasmania), and the 1989 increase, based on a linear regression, was 3.7 percent. The free tropospheric data over Europe and the North Atlantic (1978–1987) show a trend of 5.2±0.8 pptv per year or 4.5 percent per year in 1984 (Scheel et al., 1988; Seiler and Scheel, 1991). The Hokkaido data (Makide et al., 1987; Makide, 1991) show an increase of 4 pptv per year over the period 1980–1990 (2.7 percent in 1989) and 5 pptv per year over the period 1987–1990 (3.4 percent in 1989). The concentrations of CH3CCI3 observed on Hokkaido are about 15 percent lower than in Ireland or Oregon, although these differences could be due to different calibration scales (see 1.3.2).

The available data on the global distribution and trends of HCFC-22 are limited, reflecting the relative difficulty in making atmospheric HCFC-22 measurements, which can be achieved by spectroscopy (total column) or gas chromatographic techniques involving large volume air samples.

HCFC-22 data have been regularly obtained from the PNW region of the U.S. and from the South Pole (Rasmussen et al., 1980; Khalil and Rasmussen, 1981; Rasmussen and Khalil, 1982, 1983). The PNW data from 1976 to 1981 showed concentrations increasing by about 12±1 percent per year, with an absolute concentration uncertainty of ±10 percent. Combined PNW–South Pole data for 1979–1987 have recently been reported (Khalil and Rasmussen, 1990b), which show a concentration in January 1987 of 105 pptv increasing by 6.4±0.3 pptv per year or 6.1 percent in January 1987. Observations from Cape Grim (1984–1987), show a mean concentration and increase in 1987 of 91 pptv and 6.5±0.3 pptv per year, or 7.1±0.3 percent per year (Fraser et al., 1989). These data are all in the same scale (OGIST).
Figure 1-5 Methyl chloroform observations (pptv) in the four semihemispheres (GAGE: Prinn et al., 1991, 1992, UT: Makide et al., 1987 Makide, 1991. FIAER: Scheel et al., 1988; Seiler and Scheel, 1991. OGIST: Rasmussen and Khalil, 1986; Khalil and Rasmussen, 1990b.) Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: GAGE, R. Prinn; UT, Y. Makide; UEA, S. Penkett; FIAER, H. Scheel.
Figure 1-6 Northern Hemispheric, Southern Hemispheric, and global HCFC-22 observations (pptv) (PNW, South Pole: Khalil and Rasmussen, 1981; Rasmussen and Khalil, 1982, 1983; spectroscopic: Rinsland et al., 1989, 1990; Tasmania: Fraser et al., 1989; global: Khalil and Rasmussen, 1990b).
and are shown in Figure 1-6. The OGIST and UEA independent HCFC-calibration 22 scales agree to within 5 percent (Rasmussen et al., 1980).

Solar spectroscopic HCFC-22 measurements from Kitt Peak, AZ (32°N), over the period 1980-1988 show an increase of 7.8±1.0 percent per year, with an absolute error of ±25 percent, arising largely from the uncertainty in the HCFC-22 spectroscopic parameters (Rinsland et al., 1989). These parameters have been refined, and derived concentrations increased by about 30 percent, resulting in reasonable agreement between spectroscopic and gas chromatographic measurements. Additional data from balloon-borne spectrometers and Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) at 31-32°N (<15km) have been obtained (Rinsland et al., 1990) and the combined data are shown in Figure 1-6. The combined data show a mean concentration in 1989 of 93 pptv and an increase of 5.8±0.4 pptv per year or 6.2 percent per year, based on a linear regression. A trend of =10 percent per year has been reported from stratospheric observations for the period 1982-1987 (Fabian et al., 1989).

The long-term stability of the OGIST CH3CCl3 standard has been possibly but not absolutely demonstrated by extensive, periodic internal comparisons of several original ALE-GAGE calibration gases and by a comparison of measurements made in 1978-1979 in the ALE-GAGE program in Tasmania with modern measurements on air archived from that period. These experiments limit the magnitude of a calibration drift component of the observed trend to about 0.2 percent per year, comparable to the uncertainty in the long-term trend due to measurement variability (Prinn et al., 1992).

1.3.3 Methylchloroform Lifetime and the Global OH Abundance

A three-dimensional model has been used to compute tropospheric OH levels from observations of CH4, CO, O3, and NOx (Spivakovsky et al., 1990a) and used to simulate the global distribution of CH3CCl3 (Spivakovsky et al., 1990b). The computed OH fields result in a model CH3CCl3 lifetime of 5.5 years. The observed CH3CCl3 annual cycle south of 25°S is dominated by seasonal changes in OH (CH3CCl3 sink), whereas the seasonal variation of CH3CCl3 in the tropics and at northern mid-latitudes are dominated by the effects of transport.

The measured ALE–GAGE trends of CH3CCl3 have been combined with industrial emission estimates (Midgley, 1989) to deduce a globally averaged CH3CCl3 lifetime of 5.7 (+0.7, -0.6) years and an average tropospheric OH concentration of (8.7±1.0) x 10^5 radicals per cm³ (Prinn et al., 1992).

Theoretical (Wine and Chameides, 1990) and observational (Butler et al., 1991) studies have suggested that the ocean is a significant sink for CH3CCl3. The data of (Butler et al. 1991) imply that OH levels computed from CH3CCl3 data are 5–10 percent too high if the oceanic sink is ignored. Incorporating an oceanic sink into the GAGE CH3CCl3 inversion study results in a lower average OH level of (8.1±0.9) x 10^5 radicals per cm³ (Prinn et al., 1992).
The ALE-GAGE CH$_3$CCI$_3$ trend implies that the globally averaged OH levels have been increasing over the period 1978–1990 by 1.0±0.8 percent per year (Prinn et al., 1992). The deduced positive OH trend is qualitatively consistent with predicted changes in tropical tropospheric OH and O$_3$ driven by tropical biomass burning (Keller et al., 1991). This possible trend in OH has major implications for other trace gases that are primarily removed by reaction with OH, e.g., CH$_4$, CO, HCFC-22 and other HCFCs and HFCs.

1.3.4 HCFC-22 lifetime

A three-dimensional model simulation of HCFC-22 estimates the lifetime of HCFC-22 to be 15.5 years (Golombek and Prinn, 1989). With emissions increasing from about 100 million kg per year in 1977 to 220 million kg per year in 1985, good agreement is obtained between observations and model results at Cape Grim in 1984. There is a tendency for the model to overestimate the Cape Grim trend, which is probably due to an overestimation of emissions and/or an underestimation of absolute HCFC-22 concentration.

1.4 OTHER CHLORINATED SPECIES

1.4.1 Methyl Chloride

There have been no data, further to (WMO, 1990a), reported on the global distribution of methyl chloride (CH$_3$Cl). A global average background concentration of ≈600 pptv is assumed.

1.4.2 Chloroform

Chloroform measurements have been made regularly at Cape Grim as part of the OGIST flask sampling program and as part of the GAGE in situ measurement program. The GAGE data have been calibrated with respect to a NIST SRM (Fraser, 1991). The global background concentration in 1989 was ≈10 pptv, based on the previously reported ratio of Northern to Southern Hemispheric measurements (Khalil and Rasmussen, 1983b). Approximately 40 percent of the CHCl$_3$ source required to maintain the observed global concentration (400 million kg per year) is anthropogenic (Khalil and Rasmussen, 1983b). Termite mounds were found to contain elevated levels of CHCl$_3$, which were calculated to emit 100 million kg per year (Khalil et al., 1990).

1.5 HALONS AND OTHER BROMINATED SPECIES

Bromine enters the atmosphere through various processes, both natural and anthropogenic. The bromine source gases that are present in the troposphere are shown in Table 1-1.

The most abundant is methyl bromide (CH$_3$Br), which has both natural and anthropogenic sources. The main natural sources of CH$_3$Br are oceanic biological processes (mainly algal), where it is formed with other hydrogen-containing molecules, such as CH$_2$Br$_2$, CHBr$_3$, CH$_2$BrCl, and CHBrCl$_3$. However, measurements of CH$_3$Br made over the Atlantic Ocean show a marked interhemispheric gradient, with average concentrations of 15 pptv and 10 pptv being recorded in the Northern and Southern Hemispheres respectively (Penkett et al., 1985). This argues for a substantial land-based source, which could well be anthropogenic. The source strength required to produce the observed abundance is 100 million kg per year, whereas the annual anthropogenic production is about 20 million kg (SORG, 1990). There may be other unaccounted sources of anthropogenic CH$_3$Br.

Observational data records of sufficient frequency and duration to determine possible trends in atmospheric bromine species are rare. The available halon data from the OGIST flask sampling network up to 1986 were recently summarized (WMO, 1990a), which suggested global mean concentrations and rates of increase of 1.7 and 2.0 pptv and 12 and 15 percent per year respectively for CBrClF$_2$ and CBrF$_3$. Thompson et al. (1990) have reported NOAA-CMDL shipboard data in 1987 and 1989 of 1.6 and 1.8 pptv, increasing at 8 and 25 percent per year respectively for CBrClF$_2$ and CBrF$_3$.

Rasmussen, et al. (1990) has recently revised the global growth rates from the OGIST flask network to be =15 and =20 percent per year respectively for CBrClF$_2$ and CBrF$_3$, but absolute concentrations were not reported. Based on the 1986 data and the latest growth rates, the concentrations expected in 1989 for CBrClF$_2$ and CBrF$_3$ would be 2.5 and 3.5 pptv respectively. Singh et al. (1988) reported tropospheric
SOURCE GASES

Concentrations for CBrClF₂ and CBrF₃ at the mid-latitudes of the Northern Hemisphere in 1987 of 2.0 and 1.3 pptv respectively. The CBrClF₂ data compare favorably with the OGIST Northern Hemisphere data (WMO, 1990a), but the CBrF₃ data are ≈50 percent lower. These data from three independent laboratories (OGIST, NOAA–CMDL, and Max Planck Institute for Aeronomy, or MPIA) suggest that the uncertainties in calibration of CBrClF₂ and CBrF₃ are ≈±15 percent and ≈±40 percent respectively.

1.6 CARBONYL SULPHIDE

Chlorine-catalyzed O₃ destruction may be enhanced by heterogeneous processes on the ubiquitous stratospheric aerosol layer (Brasseur et al., 1990). In times of low volcanic activity this stratospheric aerosol layer (sulphate) is maintained by an upward flux of gaseous sulphur precursors, mainly carbonyl sulphide (COS), which are either oxidized or photolyzed in the stratosphere (Crutzen, 1976), while volcanic injections supply sulphur to the stratosphere mainly as sulphur dioxide (SO₂) during individual volcanic eruptions.

COS is the most abundant sulphur gas in the remote atmosphere. Global background concentrations of COS are 5×10⁻¹⁴ pptv (Khalil and Rasmussen, 1984b). The major sources are the oceans (20–40 percent), via the photooxidation of organic material (Ferek et al., 1989), anthropogenic activities (20 percent), biomasses burning (10 percent) and the oxidation of carbon disulphide (CS₂) (30 percent), while the major sinks are vegetation (≈80 percent), tropospheric oxidation (≈10 percent) and stratospheric loss (≈10 percent) (Khalil and Rasmussen, 1984b; Servant, 1989). Estimates of the atmospheric lifetime range from 2 to 6 years.

1.7 NITROUS OXIDE

Nitrous oxide is an important component of the background atmosphere, being a climatically significant species and the major source of stratospheric nitrogen oxides, which are significant in regulating stratospheric ozone.

Nitrous oxide is a long-lived atmospheric species, with a lifetime in excess of 150 years (Prinn et al., 1990), whose dominant source is believed to be denitrification in aerobic soils, which has a significant anthropogenic component (deforestation and the use of nitrogenous fertilizers). Biomass burning and fossil fuel combustion are now believed to be only small N₂O sources, although biomass burning may affect subsequent soil N₂O releases (Anderson et al., 1988; Prinn et al., 1990; IPCC, 1990). The oceans are significant sources of N₂O, which vary considerably with location and ocean circulation processes (Butler et al., 1989; IPCC, 1990). The major sinks for N₂O are stratospheric photodissociation and photooxidation.

1.7.1 Atmospheric Distributions and Trends

There are several long-term measurement programs studying N₂O. Shipboard and ground-based measurements have been regularly made by Scripps Institution for Oceanography (SIO) since 1976 (Weiss, 1981; WMO, 1990a). NOAA–CMDL and ALE–GAGE have operated independent five-station networks covering both hemispheres since 1977 and 1978 respectively (Thompson et al., 1990; Prinn et al., 1990). Long-term N₂O measurement programs have been carried out at Cape Point since 1983 (Brunke et al., 1990; Scheel et al., 1990) and in the PNW of the United States and at the South Pole since 1975 (Rasmussen and Khalil, 1986; Khalil and Rasmussen, 1990). Mid-tropospheric N₂O data have been obtained by aircraft air sampling over Japan (33°–38°N) since 1983 by Meteorological Research Institute (MRI) (Hirota et al., 1988; Hirota and Sasaki, 1991) and over Europe and the North Atlantic by FIAER since 1979 (Scheel et al., 1988).

The available data are shown in Figure 1–7 divided into the four semihemispheres, as well as global data derived by averaging spline fits to the individual CMDL and ALE–GAGE station data sets. From the SIO data (1976–1987) (not shown) a global average concentration and increase (1986) of 304.8 ppbv and 0.61±0.04 ppbv per year or 0.20 percent per year have been deduced (WMO, 1990a). The NOAA–CMDL data (1977–1989) show a global concentration and increase for 1989 of 308.5 ppbv and 0.64±0.06 ppbv per year or 0.21 percent per year (Thompson et al., 1990). The ALE–GAGE data (1978–1989) show a global concentration in 1988 of 307.2 ppbv and an increase (1978–1988) of 0.25–0.31 percent per year (Prinn et al., 1990). The 1989 global mean was 307.0 ppbv (mean of Northern Hemisphere (Ireland, Barbados) and Southern Hemisphere (Tasmania) (Prinn et al., 1991). The Cape Point data (1983–1988) show...
Figure 1-7 Nitrous oxide observations (ppbv) in the four semihemispheres (NOAA: Thompson et al., 1990. OGIST: Khalili and Rasmussen, 1990b) Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: NOAA, J. Elkins; GAGE, R. Prinn; FIAER, H. Scheel.
SOURCE GASES

an increase of 0.6±0.1 ppbv per year or 0.21 percent per year in 1984 (Brunke et al., 1990; Scheel et al., 1990), while the PNW–South Pole data show an increase of 1.0±0.1 ppbv per year or 0.34 percent per year in January 1985 (Rasmussen and Khalil, 1986). The global data from the OGIST network (1975–1988), (Khalil and Rasmussen, 1990b) show an average increase of 1.0±0.1 ppbv per year or 0.33 percent per year (1988).

The mid-tropospheric N\textsubscript{2}O data over Japan show an average increase (1983–1989) of 1.7±0.2 ppbv per year (Hirot a and Sasaki, 1991). The free tropospheric data over Europe and the North Atlantic between 1979 and 1987 show an annual average increase of 0.5 ppbv per year or 0.16 percent per year (1987) (Scheel et al., 1988). Spectroscopic observations of N\textsubscript{2}O from Kitt Peak between 1979 and 1985 place an upper limit on the growth rate of 0.3 percent per year (Wallace and Livingston, 1990b).

1.7.2. Global Nitrous Oxide Budgets

The ALE–GAGE data have been interpreted (Prinn et al., 1990), using inverse theory and a nine-box model of the global atmosphere, to show that the global distributions and trends are consistent with the hypothesis that stratospheric photodissociation is the major sink for N\textsubscript{2}O and that the cause of the N\textsubscript{2}O trend appears to be a combination of a growing tropical source (probably tropical land use) and a growing northern mid-latitude source (fertilizer and fossil fuel use). The N\textsubscript{2}O budget that best fits the ALE–GAGE observations (not a unique solution) is shown in Table 1-2, together with the budget produced for the IPCC (IPCC, 1990).

The IPCC budget indicates that there are probably unaccounted for or underestimated N\textsubscript{2}O sources, while the (Prinn et al.) budget is essentially balanced. The difference between the two budgets is largely due to the significant biomass burning-tropical land clearing term in the latter, resulting from large postburn, postclearing N\textsubscript{2}O emissions (Anderson et al., 1988; Luizao et al., 1989; Prinn et al., 1990). The global emissions of N\textsubscript{2}O due directly to biomass burning alone have been recently reassessed as less than 2 Tg (N\textsubscript{2}O) per year (Cofer et al., 1991) or even less than 1 Tg (N\textsubscript{2}O) per year (Crutzen and Andreae, 1990; Hao et al., 1991).

Table 1-2 The global N\textsubscript{2}O budget, Tg (10\textsuperscript{12}g) (N\textsubscript{2}O) per year (IPCC, 1990; Prinn et al., 1990; Sanhueza, 1991).

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<tr>
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</tr>
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<tr>
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</tr>
<tr>
<td>Total</td>
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<td>8–25</td>
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A revised N$_2$O budget, prepared for IPCC (Sanhueza, 1991) is also given in Table 1-2. The estimates were updated using new information on tropical soil fluxes (Sanhueza et al., 1990; Matson et al., 1990), temperate forest soil fluxes (Bowden et al., 1990), detailed evaluations of cultivated soils (Bouwman, 1990; Eigener, 1990), and new estimates from biomass burning (Lobert et al., 1990; Cofer et al., 1991). Recent results have confirmed that the N$_2$O emissions from stationary combustion sources are very low (De Soete, 1989; Linak et al., 1990; Sloan and Laird, 1990; Yokoyama et al., 1991).

Other, possibly globally significant, N$_2$O sources have been identified since the IPCC review and are included in Table 1-3. The worldwide production of nylon could contribute $<1$ Tg (N$_2$O) per year (Thiemens and Trogler, 1991), and mobile combustion sources =0.6 Tg per year (De Soete et al., 1989). The revised N$_2$O budget still indicates that there are unidentified and/or underestimated N$_2$O sources.

Some possible candidates are the use of legume pastures as nitrogenous fertilizers, which account for 15 percent of Australian N$_2$O emissions (Galbally et al., 1992) and the significant, but unidentified, emissions of N$_2$O (2-3 Tg [N$_2$O] per year), possibly from stationary sources in Europe (Prather, 1988; Simmonds and Derwent, 1991).

1.8 METHANE

Methane is an important trace gas in the global atmosphere because it absorbs infrared radiation, thus impacting on climate. Methane is involved in tropospheric chemistry via OH and O$_3$ budgets, and it impacts on stratospheric chemistry as a source of hydrogen (H$_2$) and H$_2$O and as a sink for stratospheric chlorine. Methane is produced from a variety of anaerobic processes and is primarily removed by reaction with OH in the troposphere.

1.8.1 Atmospheric Distributions and Trends

There are several long-term CH$_4$ measurement programs. Ground-based measurements at globally distributed sites have been regularly made by NOAA--CMDL (USA) since 1983 (Steele et al., 1987; Lang et al., 1990a, b), by CSIRO (Australia) since 1978 (Fraser et al., 1986a), by UCI (USA) since 1978 (Blake and Rowland, 1988), and by OGIST (USA) since 1978 (Khalil and Rasmussen, 1983a; 1990a). Long-term CH$_4$ measurement programs have been carried out at Cape Point, South Africa, since 1983 by CSIR (South Africa)--FIAER (Germany) (Brunke et al., 1990; Scheel et al., 1990), in the PNW and at the South Pole since 1975 (Rasmussen and Khalil, 1986), and at Tsukuba, Japan, since 1985 (Hirota et al., 1989). Mid-tropospheric CH$_4$ data have been obtained by aircraft air sampling over southeast Australia (Fraser et al., 1984, 1986a) since 1980 and over Europe and the North Atlantic by FIAER since 1979 (FIAER, Scheel et al., 1988).

Selected available CH$_4$ data are shown in Figure 1-8, divided into the four semi--hemispheres and the published CH$_4$ trends are summarized in Table 1-3.

The rate of methane increase has slowed during the last decade, as observed at Cape Grim, Tasmania, (1978-1983: $>$20 ppbv per year; 1983-1990: 12±2 ppbv per year; (Steele et al., 1987; WMO, 1990; Fraser, 1991) and in Antarctica (1983: 13.6 ppbv per year; 1988: 10.4 ppbv per year; (Steele et al., 1989). The observed growth rates as a function of time for the global OGIST and UCI and CSIRO Southern Hemispheric networks are shown in Figure 1-9. The data confirm high growth rates during 1978-1982 (17-21 ppbv per year), which have since declined to 8-13 ppbv per year (1988-1990). Satisfactory explanations for this rapid decline in CH$_4$ growth rates have yet to emerge.

Prinn et al. (1992) have calculated from industry emission estimates and trend observations of CH$_3$CCl$_3$ that OH levels in the tropical troposphere are increasing about 1 percent per year. If correct, this has important implications for the CH$_4$ budget. It suggests that the increasing levels of OH are as important as the approach to equilibrium in determining the slowing down in the CH$_4$ growth rate. It also allows sources to grow at 1-2 percent per year, rather than the 0-1 percent per year required if OH is constant.

Stevens (1988) has noted that the change in atmospheric CH$_4$ growth rate was accompanied by changes in its $^{13}$C composition. This was true in both the Northern and Southern Hemispheres, where there were
### Table 1-3 Global and regional CH₄ trends (ppbv per year, percent per year) from various observational networks.

<table>
<thead>
<tr>
<th>Network</th>
<th>Region/Location</th>
<th>Increase</th>
<th>Year</th>
<th>Reference</th>
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<td>1984</td>
<td>1-4</td>
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<tr>
<td>(since 1983)</td>
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<td>12.9±0.1</td>
<td>1986</td>
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<tr>
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<td>South Pole</td>
<td>11.9±0.1</td>
<td>1988</td>
<td></td>
</tr>
<tr>
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<td>Southern Hemisphere</td>
<td>18±2</td>
<td>1981</td>
<td>3,5,6</td>
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<tr>
<td>(since 1978)</td>
<td></td>
<td>18±1</td>
<td>1984</td>
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<tr>
<td></td>
<td></td>
<td>11.9±0.2</td>
<td>1986</td>
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<td>UCI</td>
<td>Global</td>
<td>16±1</td>
<td>1987</td>
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<td>1985</td>
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<td>(since 1978)</td>
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<td>1986</td>
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<td></td>
<td>Global</td>
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<td>1988</td>
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<td></td>
<td>Global</td>
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<td>1979</td>
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<td>1984</td>
<td>13</td>
</tr>
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<td>(since 1983)</td>
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<td>14</td>
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<td>(since 1985)</td>
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<td>S.E. Australia</td>
<td>20±4</td>
<td>1981</td>
<td>3,5,6</td>
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<td>(since 1980)</td>
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<tr>
<td></td>
<td></td>
<td>12±1</td>
<td>1986</td>
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<tr>
<td>FIAER</td>
<td>Europe and North Atlantic</td>
<td>12.7</td>
<td>1987</td>
<td>15</td>
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<td>(since 1987)</td>
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<td>Total Column Measurements</td>
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<td>1951-1986</td>
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<td>1979-1985</td>
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<td>1.1</td>
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<td>17</td>
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<tr>
<td>1979-1989</td>
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References:
Figure 1-8 Methane observations (ppbv) in the four semihemispheres (NOAA: Steele et al., 1987; Lang et al., 1990a, b. CSIRO: Fraser et al., 1986a, 1990; Fraser, 1991. OGIS: Khalil and Rasmussen, 1990a. UCI: Blake and Rowland, 1988; Rowland, 1990; Blake and Rowland 1991). The CSIRO (30°S–90°S) data are averages of Cape Grim (41°S) and Mawson (67°S) data. Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: CSIRO, P. Fraser; UCI, D. Blake.
Figure 1-9 The global and Southern Hemispheric CH$_4$ trends from 1978–1990. The trends are obtained from spline fits to the long-term CH$_4$ data records (Blake and Rowland, 1988, 1991; Rowland, 1990; Khalil and Rasmussen, 1990a; Fraser et al., 1986a, 1990; Fraser, 1991).
reductions in the $^{13}$C depletion. These changes have been tentatively interpreted as indicating that there were changes in the source distribution of CH$_4$ (probably in the Northern Hemisphere) that were not of anthropogenic origin. It was suggested that there may have been a decrease in the flux of isotopically light (more $^{13}$C-depleted) CH$_4$ of natural origin, such as that from wetlands.

Recent results from a high-accumulation-rate ice core (Etheridge et al., 1992) show that there have been significant variations in the CH$_4$ growth rate over the period 1840–1980, with accelerating growth from 1890 ($<$0.2 percent per year) to 1925 (0.5 percent per year), approximately constant growth from 1925 to 1950 ($=0.5$ percent per year), followed by accelerating growth from 1950 (0.5 percent per year) to 1975 ($=1$ percent per year). This pattern appears to correlate with the changing production rates of fossil fuels (Keeling, 1973; Marland and Rotty, 1984), perhaps indicating a significant role for this CH$_4$ source in determining global CH$_4$ growth rates.

1.8.2 Methane Sinks

The dominant removal process for atmospheric CH$_4$ is reaction with OH. A new measurement (Vaghjiani and Ravishankara, 1991) of the rate coefficient for the reaction of OH and CH$_4$ found it to be approximately 25 percent lower than reported previously, implying that the OH-CH$_4$ sink is approximately 420 Tg per year.

The magnitude of the OH-CH$_4$ sink is estimated from models whose OH fields are calibrated by the estimated releases and observed trends of methyl chloroform (CH$_3$CCl$_3$, see 1.3.3). A further uncertainty in the magnitude of the OH-CH$_4$ sink has resulted from theoretical (Wine and Chameides, 1990) and observational (Butler et al., 1991) studies suggesting a biological or physical sink for CH$_3$CCl$_3$ in oceanic surface waters, which, if confirmed, could further reduce calculated OH levels (and the OH-CH$_4$ sink) by 10–20 percent.

Modeling studies suggest that OH levels, and hence the relative strength of the CH$_4$ sink, in preindustrial times were higher than at present. Studies of the ratio of formaldehyde (HCHO), a CH$_4$ oxidation product, to CH$_4$ in polar ice cores suggest that OH levels in preindustrial times were 30 percent higher than at present (Staffelbach et al., 1991).

Studies in Arctic, temperate, and tropical environments have firmly established the importance of a global soil sink for atmospheric CH$_4$ (Steudler et al., 1989; Keller et al., 1990; Mosier et al., 1991; Crill, 1991; Whalen and Reeburgh, 1990). However, there is considerable uncertainty associated with the magnitude of the soil sink for methane (5–60 Tg per year) (Born et al., 1990). The destruction of CH$_4$ in soils is a biological process that is sensitive to both climatic variations and land use changes. Recent CH$_4$ soil flux measurements indicate that changes in land use or enhanced nitrogen input to soils by fertilization and/or deposition of atmospheric nitrogen are decreasing the CH$_4$ uptake by soils (Scharffe et al., 1990; Mosier et al., 1991).

1.8.3 Methane Sources

A recently identified CH$_4$ source that has not been considered previously is emissions from waste water and animal waste treatment facilities (40–65 Tg per year) (Harriss, 1991). Animal wastes contribute 20–30 Tg per year (Casada and Shafley, 1990). The landfill source may be ameliorated by identified high CH$_4$ oxidation rates in landfill cover soils (Whalen et al., 1990). The preliminary data on CH$_4$ emissions from landfills, waste water treatment and animal wastes indicate a total emission of 85±20 Tg per year from anthropogenic waste management systems (Harriss, 1991).

Studies of the $^{14}$C and $^{13}$C isotopic composition of atmospheric CH$_4$ have been used to evaluate the contribution to total emissions made by fossil sources. Three independent estimates are (21±3) percent (Whalen et al., 1989), 25 percent (Manning et al., 1990; Lowe et al., 1991) and 16 percent (Quay et al., 1991). The latter value, combined with the reduction in the overall source inferred from the new estimate of the OH-CH$_4$ sink, would constrain the total fossil source to 90±10 Tg per year. Current estimates of CH$_4$ emissions from the production and use of oil, natural gas, and coal are compatible with this estimate for the total fossil source. Thus, the contributions of fossil sources such as CH$_4$ hydrate destabilization and the decomposition of old peat are apparently small.

For $^{13}$C, differing amounts of depletion are found for different CH$_4$ sources. Bacterially produced CH$_4$, such as that from wetlands, rice paddies, ruminants, and termites, is typically more highly depleted in $^{13}$C than is nonbacterial CH$_4$, such as that produced in biomass burning and in emissions of natural gas. Consideration
SOURCE GASES

of the observed $^{13}$C depletion in CH$_4$ sources together with that of atmospheric CH$_4$ and the $^{12}$C-$^{13}$C fractionation factor associated with the reaction of CH$_4$ and OH indicates that bacterial CH$_4$ makes up some 70 percent of CH$_4$ sources (Quay et al., 1991).

Methane emission rates from Chinese rice paddies (total emissions: 30 Tg per year, Khalil et al., 1991) were found to be 4-10 times higher than from U.S. and European rice fields. Matthews et al. (1991) calculate Chinese and Indian CH$_4$ emissions from rice production of approximately 20 and 30 Tg per year respectively, assuming a global rice CH$_4$ source of 100 Tg per year (Fung et al., 1991). By contrast, recent results from the major rice producing areas of India and Japan (Parashar et al., 1991; Mitra, 1991; Yagi and Minami, 1990) indicate emissions that are not significantly different from the U.S. and European data. The Indian data indicate an annual CH$_4$ flux of only 3-4 Tg per year, an order of magnitude lower than calculated above. Large rice emissions from China and India are consistent with a global rice source of about 100 Tg per year, which is in agreement with constraints imposed by atmospheric observations (Fung et al., 1991, see below). Based on the latest Indian data, Sanhueza (1991) has adopted a lower estimate of CH$_4$ emissions from rice agriculture (60 Tg per year) for the IPCC review of global CH$_4$ emissions. R. Cicerone (private communication) estimates that the uncertainty in global emissions from rice is still very large (= a factor of seven).

1.8.4 Global Methane Budgets

The NOAA global CH$_4$ data base have been interpreted with a three-dimensional model incorporating geographic and seasonal emission distributions of the major CH$_4$ sources and sinks (Fung et al., 1991). Various source and sink scenarios were tested, constrained by the observed geographic and seasonal CH$_4$ distributions and the observed $^{13}$C and $^{14}$C composition of atmospheric CH$_4$. A preferred, but not necessarily unique, budget for CH$_4$ was derived, which is shown in Table 1-4 along with that derived for IPCC (IPCC, 1990) and also recently by Crutzen (1991), Harriss

Table 1-4 The global CH$_4$ budget (Tg (CH$_4$) per year). The numbers in parentheses are the range of uncertainties in sources and sinks. Adapted from: Fung et al. (1991); IPCC (1990); Crutzen (1991); Harriss (1991); Sanhueza (1991).

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<td>115 (100-200)</td>
<td>115 (165-)</td>
<td>110 (60-160)</td>
<td>115 (100-200)</td>
</tr>
<tr>
<td>Rice</td>
<td>100 (60-170)</td>
<td>110 (25-170)</td>
<td>100 (-265)</td>
<td>100 (50-150)</td>
<td>60 (200-100)</td>
</tr>
<tr>
<td>Animals</td>
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<td>80 (65-100)</td>
<td>80 (65-100)</td>
<td>80 (65-95)</td>
<td>80 (65-100)</td>
</tr>
<tr>
<td>Fossil fuels</td>
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<td>80 (45-100)</td>
<td>95 (75-115)</td>
<td>90 (80-100)</td>
<td>95 (80-120)</td>
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<tr>
<td>Biomass burning</td>
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<td>40 (20-80)</td>
<td>30 (15-45)</td>
<td>30 (15-45)</td>
<td>30 (20-80)</td>
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<td>Land fills</td>
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<td>40 (20-70)</td>
<td>50 (30-70)</td>
<td>85 (65-105)</td>
<td>85 (65-105)</td>
</tr>
<tr>
<td>Termites</td>
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<td>40 (10-100)</td>
<td>20 (10-100)</td>
<td>20 (5-50)</td>
<td>20 (5-50)</td>
</tr>
<tr>
<td>Oceans</td>
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<td>10 (5-20)</td>
<td>10 (5-20)</td>
<td>10 (5-20)</td>
<td>10 (5-20)</td>
</tr>
<tr>
<td>Others</td>
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<td>5</td>
<td>50 (25-75)</td>
<td>10 (1-30)</td>
<td></td>
</tr>
<tr>
<td>Total</td>
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<td>525 (290-960)</td>
<td>505 (370-720)</td>
<td>545 (360-730)</td>
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</thead>
<tbody>
<tr>
<td>Chemical loss</td>
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<td>500 (400-600)</td>
<td>430 (350-510)</td>
<td>430 (345-515)</td>
<td>430 (350-510)</td>
</tr>
<tr>
<td>Soils</td>
<td>10 (5-60)</td>
<td>30 (15-45)</td>
<td>30 (15-45)</td>
<td>30 (15-45)</td>
<td>30 (15-45)</td>
</tr>
<tr>
<td>Atmospheric</td>
<td>45 (40-50)</td>
<td>45 (40-50)</td>
<td>45 (40-50)</td>
<td>45 (40-50)</td>
<td>45 (40-48)</td>
</tr>
<tr>
<td>Increase</td>
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<tr>
<td>Total</td>
<td>505 (450-605)</td>
<td>575 (455-695)</td>
<td>505 (405-605)</td>
<td>505 (400-610)</td>
<td>505 (405-605)</td>
</tr>
</tbody>
</table>

1.24
(1991), and Sanhueza (1991). The global CH₄ budget is an underdetermined problem where there are more sources and sinks than there are observations to constrain them. The largest uncertainties in CH₄ emissions are associated with landfills, tropical swamps, rice fields, biomass burning, and termites, due to a lack of direct measurements of fluxes in regions were these sources are concentrated.

In contrast to the IPCC CH₄ budget, there is now fairly good agreement between CH₄ sources and sinks plus atmospheric accumulation. This is due largely to the revised (25 percent lower) atmospheric consumption of CH₄ by OH radicals (Vaghjiani and Ravishankara, 1991). However, there still remains considerable uncertainty associated with the global methane budget. Recent estimates of methane emissions from animal wastes and waste water treatment are included in Table 1-3 only in the Harriss (1991) and Sanhueza (1991) budgets, under landfills. A possibly large methane source from asphalt (Sackett and Barber, 1988), now appears to be less than 1 Tg per year (Tyler et al., 1990).

1.9 HYDROGEN

Oxidation of H₂ in the stratosphere may affect stratospheric O₃ by supplying H₂O vapor to the stratosphere, in addition to that derived from H₂O transported from the troposphere and CH₄ oxidation.

1.9.1 Global Distribution and Trends

Measurement of H₂ in air samples collected in the OGIST global flask sampling program between 1985 and 1989 shows that the concentration of H₂ has increased by 3.2±0.5 ppbv per year (Khalil and Rasmussen, 1990e). The global average concentration in 1989 was 515 ppbv, based on the global trend and the 1988 average concentration. The concentration of H₂ in the Southern Hemisphere is about 3 percent higher than in the Northern Hemisphere. The Cape Grim data (1984–1987) from the OGIST network have been reported separately (Fraser et al., 1989).

1.9.2 Sources and Sinks

The global source and sink of H₂ is estimated to be about 90 Tg per year (Khalil and Rasmussen, 1990e), the major sources being CH₄ oxidation (30 percent), oxidation of NMHCs (25 percent), anthropogenic activities (20 percent) and biomass burning (15 percent). The major sinks are removal by soils (85 percent) and oxidation by OH (15 percent). The increasing concentration of H₂ in the atmosphere is probably due to growing sources, for example, the observed CH₄ trend may account for 50 percent of the observed H₂ trend. The higher H₂ concentrations in the Southern Hemisphere compared to the Northern Hemisphere have been interpreted as indicating that the soil sink is the dominant cause of the interhemispheric difference. The observed seasonality in the Southern Hemisphere possibly reflects the local production by CH₄ and NMHC oxidation, while the seasonality in the Northern Hemisphere may reflect the seasonality in the soil sink (Khalil and Rasmussen, 1989).

1.10 CARBON MONOXIDE

Carbon monoxide (CO) is an important trace gas in the troposphere because it plays significant roles in controlling the chemistry of ozone production and hydroxyl radical destruction in the lower atmosphere. It directly affects the oxidizing capacity of the lower atmosphere and can thus influence the concentrations of other important trace gases such as CH₄, CH₃CCl₃, and the HCFCs.

1.10.1 Atmospheric Distributions and Trends

Because of its short residence time (2–3 months), coupled with an inadequate ground-based observational network, the determination of global average concentrations and long-term trends for CO is difficult. Due to larger sources in the Northern Hemisphere, the concentration of CO in the background, marine atmosphere is a factor of about two greater than in the Southern Hemisphere, where the annual average for the background, marine atmosphere is about 50–60 ppbv.

However, over continental sites in both hemispheres, even in clean air, CO concentrations are elevated and highly variable. For example, in the Southern Hemisphere average concentrations of about 100 ppbv over tropical Brazil are typical (Kirchhoff et al., 1989; Kirchhoff and Marinho, 1989).
Remote sensing from space provides a global picture of CO spatial variability (Reichle et al., 1990), indicating large biomass burning sources over South America and tropical Africa, which presumably influence the local production of tropospheric ozone, which is subsequently transported over a significant portion of the Southern Hemisphere (Watson et al., 1990). Long-term CO data are not yet available from space platforms.

There are several long-term CO measurement programs. Ground-based measurements at globally distributed sites have been regularly made by OGIST since 1978 (Khalil and Rasmussen, 1988) and CSIRO since 1980 (Fraser et al., 1986a, b). Long-term CO measurement programs have also been carried out at Cape Point since 1979 (Brunke et al., 1990; Scheel et al., 1990). In the tropics, CO measurements have been made systematically since 1987 in the Brazilian savanna region. Besides a permanent station at Cuiaba (16°S), another station at Natal (6°S) is also maintained for reference (Kirchoff and Rasmussen, 1990).

Mid-tropospheric CO data have been obtained by aircraft air sampling over southeast Australia (Fraser et al., 1986 a, b) since 1980 and over Europe and the North Atlantic by the FIAER since 1979 (Scheel et al., 1988).

Selected available CO data are shown in Figure 1-10, divided into the four semi-hemispheres. The FIAER–CSIRO and CSIRO long-term data in the Southern Hemisphere (Cape Point, 1979–1988; Cape Grim, 1978–1991; middle troposphere, southeastern Australia, 1980–1991; Mawson, 1980–1990) do not show statistically significant trends (Fraser and Coram, 1990; Brunke et al., 1990; Scheel et al., 1990; WMO, 1990b). An earlier report of a significant CO growth at Mawson (1.5±0.6 ppbv per year) (Fraser et al., 1986a) was later proved to be an artifact of the relatively short data record. By contrast, from the OGIST network (Khalil and Rasmussen, 1988, 1990c) a CO trend in the Southern Hemisphere of 0.8±0.4 ppbv per year over the period 1980–1988 has been reported. The Northern Hemisphere data from the OGIST network show a similar positive trend (0.8±0.4 ppbv per year or 0.8–1.4 percent per year) (Khalil and Rasmussen, 1988).

A comparison of spectroscopic data recorded at Jungfraujoch Station, Switzerland, in 1950–1951 with data collected at the same site in 1985–1987 indicates increasing CO levels (0.9±0.2 percent per year, 1950–1987), assuming an exponential growth in CO over this period (Zander et al., 1989b). Spectroscopic data collected at a frequency of about six times per year at Kitt Peak do not show a statistically significant trend for the period 1978–1986 (Wallace and Livingston, 1990b).

It is clear from the long-term ground-based and mid-tropospheric records in the Southern Hemisphere that the rate of CO change exhibits complex intrannual variability. Figure 1-11 shows the rate of CO change as a function of time. Between 1978 and 1983, CO concentrations grew about 1 ppbv per year. From 1983 to 1985, CO concentrations declined, on average, 2 ppbv per year; 1986–1988: CO increased by 2 ppbv per year; 1988–1990: CO declined by 3 ppbv per year. Over the period 1978–1990, the overall trend of CO in the mid-to-high latitudes of the Southern Hemisphere is not significantly different from zero.

1.10.2 Carbon Monoxide Calibration

There has been significant progress in the calibration of CO measurements. (Weeks et al. 1989) have compared an ambient concentration OGIST calibration gas used in the CSIRO CO program to a dynamically-diluted NIST (formerly NBS) SRM (#2612a, 9.7 ppmv CO in air) and found that ambient levels of CO in the Southern Hemisphere in the NIST scale are =30–40 percent higher than those reported in the OGIST scale (=35–55 ppbv). The CSIRO data reported here (Figure 1-10) are in the NIST scale. Note that there is now good agreement between FIAER and CSIRO measurements at similar latitudes in the Southern Hemisphere. The FIAER CO scale has been found to be within 4 percent of the NIST scale (Brunke et al., 1990). The OGIST scale has recently been revised such that CO concentrations are now reported 20 percent higher than previously (Khalil and Rasmussen, 1990d). A comparison of NIST (U.S.) and National Physical Laboratory (NPL) (U.K.) gravimetric standards indicates agreement to within 0.2 percent at a range of concentrations from 10 ppmv to 8 percent (Hughes et al., 1991). Novelli et al. (1991) at NOAA–CMDL have prepared two series of gravimetric standards of CO in air at 25 to 1,000 ppbv, from pure CO as well as from a NIST SRM at 9.7 ppmv. The two sets of standards
Figure 1-10 Carbon monoxide observations (ppbv) in the four semihemispheres. All data are from the CSIRO global flask network (Fraser et al., 1986a, b; Fraser, 1991), except Cape Point (CSIR-FIAER: Brunke et al., 1990; Scheel et al., 1990). Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: CSIRO, P. Fraser; FIAER, H. Scheel.
Figure 1-11 The Southern Hemispheric CO trends from 1978–1990. The trends are obtained from spline fits to the long-term CO data records (CSIRO: Fraser et al., 1986a, b; Fraser, 1991. CSIR-FIAER: Brunke et al., 1990; Scheel et al., 1990)
agree to within 1 percent. Comparison of the OGIST and NOAA-CMDL scales at CSIRO showed that CO concentrations determined using the NOAA-CMDL scale are ≈25 percent higher than those obtained in the OGIST scale (before the 20 percent revision).

In summary, the NIST, NPL, and NOAA-CMDL CO standards agree to within 1 percent. The FIAER scale is within 4 percent of NIST, and the revised OGIST scale appears to be within 10–15 percent of the NIST scale.

1.10.3. Global Carbon Monoxide Budgets

At present, there are several uncertainties in evaluating the sources and sinks of atmospheric CO. Carbon monoxide concentrations show a large degree of spatial (Reichle et al., 1990) and temporal (Khalil and Rasmussen, 1988) variability, especially in the Northern Hemisphere over continental regions, which has not yet been adequately described by observational data. This presents serious problems in budget sensitivity studies when trying to match observations and model results (Fraser et al., 1986b). The various CO concentration data sets reported to date in the literature are probably not known to better 10 percent in an absolute sense. According to Lelieveld and Crutzen (1991), the oxidation of formaldehyde (HCHO) in the liquid phase does not produce CO but CO₂ directly. Thus, the fraction of CH₄ and higher NMHCs that produce CO during the oxidation process need to be reevaluated.

Despite these uncertainties in evaluating CO budgets, there have been several attempts to produce global budgets for CO (Table 1-5). The total emissions of CO are probably between 2,000 and 3,000 CO Tg per year, with as much as 2/3 being produced from anthropogenic activities, combustion processes (biomass (30 percent) and fossil fuel (20 percent)) being the dominant sources.

It is interesting to speculate why CO levels are not increasing in the Southern Hemisphere when CO sources are so strongly anthropogenically influenced. However, it is not obvious that all of the anthropogenic CO sources are increasing with time. Data on the temporal change of the magnitude of the biomass

<table>
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<tr>
<th>Table 1-5 The global CO budget, Tg per year.</th>
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<tr>
<td>Sources</td>
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<td>Primary</td>
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<td>440</td>
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<td>80</td>
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<td>50</td>
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<td>Secondary</td>
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<td>stratosphere accumulation</td>
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<td>Total</td>
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burning source are not readily available and the CO levels in urban areas of the developed countries appear to have declined over the past decade due to cleaner combustion processes (IPCC, 1990). The possibility of increasing levels of OH radical (Prinn et al., 1991a) also complicates the prediction of CO trends.

Crutzen and Zimmerman (1991) have developed a preindustrial CO emission scenario of about 1,000 Tg CO per year, which in a two-dimensional model simulation results in preindustrial CO levels that are 50 percent (Southern Hemisphere) to 60 percent (Northern Hemisphere) of current model levels (2,300 Tg per year CO emissions).

1.11 NON-METHANE HYDROCARBONS (NMHCs)

NMHCs could possibly play a significant role in determining the OH radical concentration in the remote marine boundary layer (Bonsang et al., 1988; Donahue and Prinn, 1990) and act as a significant source of CO. Because of their role in OH chemistry, NMHCs are important in assessing the significance of the OH sink for CH4, CO, CH3CCI3, as well as the HCFCs and HFCs.

The number of NMHCs in the background atmosphere is quite large (in excess of 100), including saturated, unsaturated, and aromatic compounds. The NMHCs can be classified by their atmospheric lifetimes:

- relatively long-lived (lifetimes > week), where the highest concentrations (up to 3 ppbv for ethane (C2H6)) are observed in the middle to high northern latitudes;
- more reactive (lifetimes between 12 hours and a week), such as C2-C5 alkenes, whose concentrations exhibit significant temporal and latitudinal variability from <0.1 ppbv in remote areas to a few ppbv close to source regions;
- extremely short-lived (lifetimes of hours) such as terpenes or isoprene whose local concentrations only may reach about 10 ppbv close to their sources.

With the exception of C2H6, trends in the atmospheric concentrations of NMHCs have not been established. Recently (Ehhalt et al., 1991) have reported a secular trend in the tropospheric concentration of C2H6 over the Northern Hemisphere of 0.9±0.3 percent per year, based on spectroscopic observations made at Jungfraujoch in 1951 and from 1984 to 1988, probably due to anthropogenic activities such as the use of fossil fuels and biomass burning.

1.11.1 Sources and Sinks for NMHCs

The oceans are a major source of NMHCs, mainly alkenes. Estimates of the source strength of ethene and propene range from =30 to 100 Tg C per year (Penkett, 1982; Bonsang et al., 1988). Emissions of NMHCs from terrestrial vegetation are species dependent, isoprene coming largely from deciduous plants (=500 Tg C per year) and terpenes from conifers (=500 Tg C per year) (Rasmussen and Khalil, 1988). These emission estimates are very uncertain. Grasslands emit 50 Tg C per year of light alkenes and higher hydrocarbons (Warneck, 1988). Anthropogenic emissions are 60 Tg C per year (Warneck, 1988) and biomass burning, 25 Tg C per year (Crutzen and Andreae, 1990). All these emissions have uncertainty factors of 2-3.

It has been generally accepted that the dominant loss mechanism for most NMHCs is reaction with the hydroxyl radical (OH). Other oxidants capable of removing hydrocarbons are ozone (O3), the nitrate radical (NO3), and chlorine atoms (Cl). Unsaturated hydrocarbons react rapidly with O3 and NO3 such that the atmospheric lifetimes of isoprene for removal by OH, O3, and NO3 are 18 hours, 1.2 days, and 20 hours respectively; for a terpene such as α-pinene the lifetimes are respectively 3.4 hours, 4.6 hours, and 2 hours (Corchnoy and Atkinson, 1990). It has also been proposed that chlorine atoms may remove large proportions of some saturated hydrocarbons such as ethane and propane (Singh and Kasting, 1988). This appears to be much less likely now after the findings of low HCl concentration (the source of the Cl atoms over the ocean) (Harris et al., 1991).

To improve our understanding of the role of NMHCs in the tropospheric OH chemistry, a global observational data base of the unsaturated hydrocarbons (up to C8) at the 1 pptv level is required, both in the atmosphere and surface ocean waters, as well as concurrent O3, CO, and UV flux observations (Donahue and Prinn, 1990).
1.12 CARBON DIOXIDE

Next to H₂O vapor, CO₂ is the most important greenhouse gas in the atmosphere. Increasing concentrations of CO₂ are predicted to cause a warming of the troposphere and a cooling of the stratosphere, the latter resulting directly in increased levels of stratospheric O₃, or indirectly, through the formation of stratospheric aerosols, reduced levels of stratospheric O₃.

1.12.1 Atmospheric Distributions and Trends

There are several long-term measurement programs for CO₂ in the remote atmosphere. Recent publications from the NOAA-CMDL laboratory describe the results from in situ (Mauna Loa, Thoning et al., 1989; Samoa, Waterman et al., 1989) and flask observations (Conway et al., 1988). Data up to 1989 are summarized in Novelli et al. (1990).

Concentrations in the Northern Hemisphere are typically 2–3 ppmv higher than in the Southern Hemisphere of CO₂, although the difference between the hemispheres shows substantial interannual variation. The global average CO₂ concentration and increase in 1989, based on the NOAA-CMDL in situ data from Barrow, Mauna Loa, Samoa, and the South Pole, was 352.2 ppmv and 1.6 ppmv per year respectively (Novelli et al., 1990). The global average growth rate shows considerable variation from year to year, with values as high as 2.6 ppmv per year (1987–1988) and as low as 0.4 ppmv per year (1981–1982). The long-term growth rate is increasing.

Like CH₄, the observed change in CO₂ amounts has been accompanied by a change in its ¹³C composition. CO₂ has become more depleted in ¹³C as isotopically light (more ¹³C-depleted) CO₂ is added to the lighter pool of atmospheric CO₂ (Kaye et al., 1989).

Variations in atmospheric CO₂ are correlated with El Niño-Southern Oscillation (ENSO) events (Keeling et al., 1989). Some clues to the cause of this correlation may be found in ¹³C/¹²C ratios of atmospheric CO₂, which allow CO₂ of terrestrial and marine origin to be distinguished. The ¹³C/¹²C data to date are somewhat contradictory (Keeling et al., 1989; Francey et al., 1990), so that a wide range of CO₂ fluxes associated with ENSO events are possible.

1.12.2 Sources and Sinks of CO₂

The extent to which the terrestrial biota contribute to long-term changes in atmospheric CO₂ has long been a contentious question in carbon cycle studies. Inversion calculations (two-dimensional model), using surface atmospheric CO₂ observations (Enting and Mansbridge, 1989, 1991; Tans et al., 1989), and three-dimensional model studies, supplemented by analysis of surface atmospheric and oceanic partial pressure data (Tans et al., 1990), concluded that there is a large, previously unidentified sink for CO₂ in the Northern Hemisphere, probably biotic uptake. More recently, it has been appreciated that the Tans et al. (1990) analysis neglects a natural cycle of CO₂ taken up by the terrestrial biota, transported into the oceans via rivers and then outgased into the atmosphere to close the cycle (Sarmiento and Siegenthaler, 1991). The existence of this cycle represents a correction of perhaps 0.6 Gt to the net ocean uptake calculated by Tans et al. (1990). In addition, Enting and Mansbridge (1991) noted that the role of CO in the atmospheric budget implies a correction of about 0.25 Gt to budgets based in interpreting the spatial distribution of CO₂. (The correction needs to be added to southern sinks and subtracted from northern sinks.) The effect of these corrections is to bring the ocean fluxes estimated by Tans et al. (1990) into much better agreement with ocean uptake based on global-scale carbon cycle modeling. However, this still implies the need for some biotic uptake of comparable magnitude to the carbon release from deforestation. In particular, estimates of the spatial distribution of CO₂ sources show a tropical source comparable to that expected from ocean outgasing without any additional contribution from tropical deforestation.

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