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CHAPTER 8

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Trends in Source Gases

Panel Members

D. H. Ehhalt and P. J. Fraser, Co-Chairs
D. Albritton
R. J. Cicerone
M. A. K. Khalil
M. Legrand
Y. Makide
F. S. Rowland
L. P. Steele
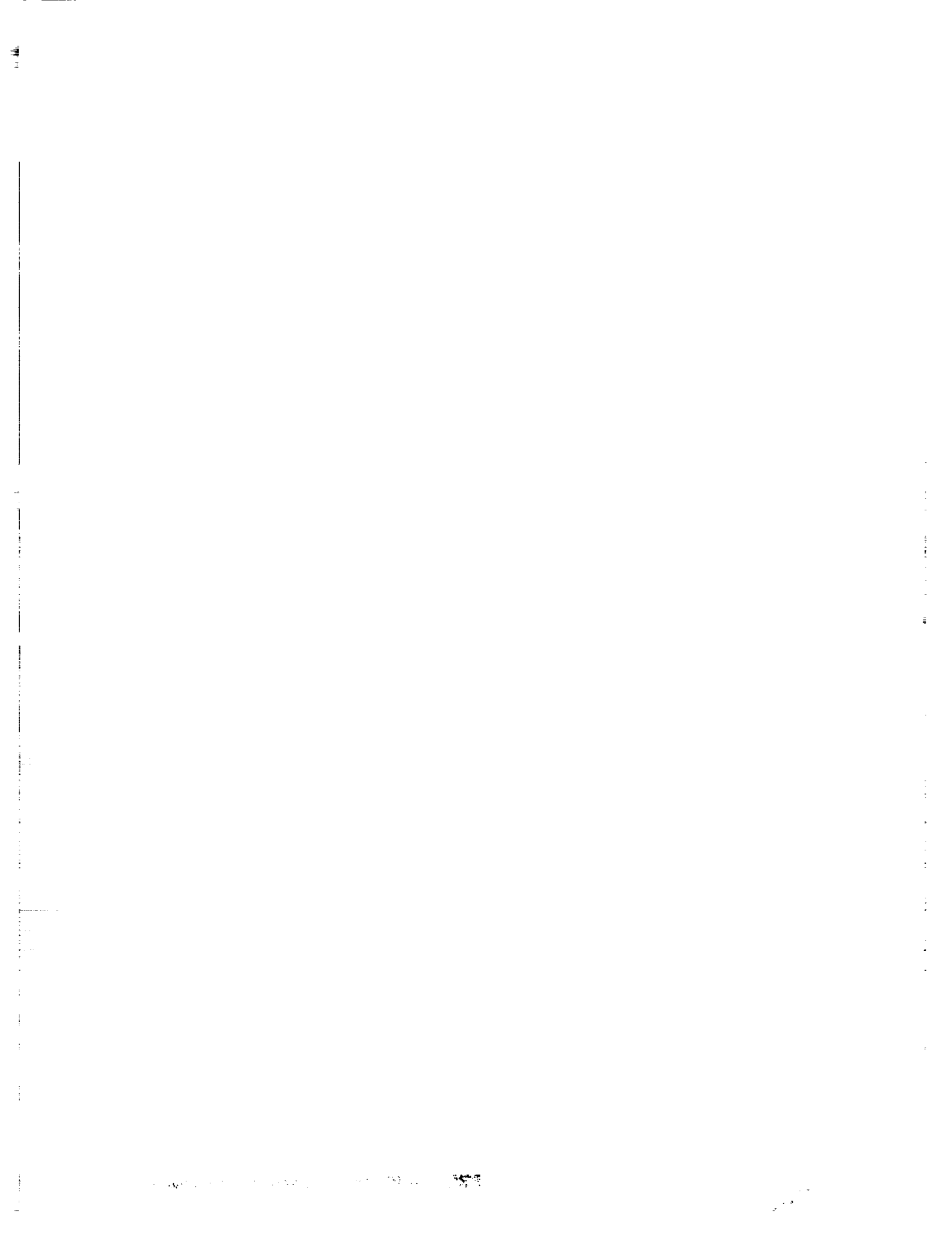R. Zander

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Chapter 8

Trends in Source Gases

Contents

8.1 INTRODUCTION

Source gases are defined as those gases that, by their breakdown, introduce into the stratosphere halogen, hydrogen, and nitrogen compounds that are important in stratospheric ozone destruction. These source gases are emitted at the Earth's surface, either naturally or anthropogenically, and are long lived in the troposphere. Many show significant and well-documented increases in their tropospheric concentrations. The following chapter updates the existing concentration time series for chlorocarbons, nitrous oxide, and methane reported in the previous review (*WMO*, 1986). It also reviews the information accumulating on other halogen-containing species and investigates these data for possible trends. As far as it exists, evidence on trends in trace gases that influence tropospheric chemistry and thus the tropospheric lifetimes of source gases, such as carbon monoxide, carbon dioxide, or nitrogen oxides, is also reviewed. As an overview, the current trends and concentrations are summarized in Table 8.1. The implications of the observed trends in terms of global sources and sinks for these compounds are not discussed in detail in this chapter; the reader is referred to the previous review (*WMO*, 1986) for a comprehensive summary of these aspects of trace gas studies.

Table 8.1 Updated Global Trends and Tropospheric Concentrations of Source Gases for 1986. Where Appropriate and Available, Lifetimes Are Also Tabulated.

Source gas	Concentration 1986 pptv	Rate of increase 1986 pptv/yr	%/yr	Lifetime[a] yr
CCl_2F_2[a]	392	16.7	4.3	111^{+222}_{-44}
CCl_3F[a]	226	9.0	4.0	74^{+31}_{-17}
CH_3CCl_3[a]	139	6.2	4.5	7 ± 1
CCl_4[a,b]	129	1.8	1.4	≈ 40
CCl_2FCClF_2[b]	32	3.6	11.3	≈ 90
$CHClF_2$[b]	92	6.5(c)	7.1	≈ 20
CH_3Cl	≈ 600	—	—	≈ 1.5
$CBrF_3$[b]	2.0	0.3	15	≈ 110
$CBrClF_2$[b]	1.7	0.2	12	≈ 25
CH_3Br[b]	10–15	?		≈ 2
N_2O	$(306 - 309) \times 10^3$	$(0.65 - 0.8) \times 10^3$	0.2–0.3	≈ 150
CH_4[d]	1638×10^3	$(13 - 16) \times 10^3$	0.8–1.0	≈ 10
CO[b]	103×10^3	(see 8.7)		0.1–0.2
CO_2[d]	345×10^6	1.2×10^6	0.4	
Total Cl[e]	3185	104	3.3	
Total F[e]	1300	67.5	5.2	
Total Br[e]	14–19	0.5	3–4	

[a] The lifetimes of the first four species have been derived from observations (see 8.2). The others are adopted from *WMO* (1986).
[b] Calibration uncertain, see 8.3.
[c] Southern Hemisphere, see 8.3.
[d] 1985 data.
[e] The total amounts include all the appropriate compounds listed in this table, which are thought to be the major species of global importance. Because of its exceedingly long lifetime, CF_4 is not included in total F.

8.2 HALOCARBONS: CCl_3F, CCl_2F_2, CH_3CCl_3, CCl_4

Measurements of the atmospheric halocarbons trichlorofluoromethane (CCl_3F, CFC–11), dichlorodifluoromethane (CCl_2F_2, CFC–12), methylchloroform (CH_3CCl_3), and carbon tetrachloride (CCl_4) have been made at a number of locations in both hemispheres. An important program in this context is the Global Atmospheric Gases Experiment (GAGE), which began in 1978 as the Atmospheric Lifetime Experiment (ALE) (Prinn et al., 1983a), and continues to the present. This program provides in situ measurements from five stations, three in the Northern and two in the Southern Hemisphere. Measurements of CCl_3F, CCl_2F_2, CH_3CCl_3, and CCl_4 have also been made on Hokkaido, Japan, since 1979, using air samples collected in stainless steel flasks (Makide et al., 1987a). Since 1977, the Geophysical Monitoring for Climatic Change laboratory (GMCC) of the National Oceanic and Atmospheric Administration (NOAA) has analysed air samples for CCl_3F and CCl_2F_2 collected in stainless steel flasks at Barrow, Alaska; Niwot Ridge, Colorado; Mauna Loa, Hawaii; Cape Matatula, Samoa; and the South Pole (GMCC, 1986a).

The GAGE data, up to mid-1984, were discussed in the previous report (WMO, 1986). Figures 8.1 to 8.4 extend the data to the end of June 1986 (Cunnold et al., 1983a,b, 1986; Prinn et al., 1983b, 1987; Simmonds et al., 1983, 1988). Average concentrations observed at each site in 1985 are shown in Table 8.2. The concentration of each gas is increasing with time. The growth rates, expressed as pptv per year (Table 8.3), averaged over the globe are 9.0(0.1) for CCl_3F, 16.7(0.1)

Table 8.2 Annual Mean Halocarbon Concentrations (pptv) Observed at the GAGE Sites in 1985. The Data Must Be Regarded as Preliminary. The Global Average Is the Mean of the Four GAGE Sites. CCl_3F Data Were Collected on a Porosil Column.

	CCl_3F	CCl_2F_2	CH_3CCl_3	CCl_4
Oregon	223.2	385.6	155.4	129.2
Barbados	221.8	381.7	141.4	129.2
Samoa	211.0	362.9	117.4	124.8
Cape Grim	210.2	361.7	116.6	124.3
Global Average	216.6	373.0	132.7	126.9

Table 8.3 Halocarbon Growth Rates (pptv/yr) Observed at the ALE–GAGE Sites Over the Period 1978 to June 1986. The Data Must Be Regarded as Preliminary. Adrigole Ceased Operation in 1984. Growth Rates Were Obtained by Least Squares Linear Regression; the Numbers in Parentheses Are Single Standard Deviations. The Global Average is the Mean of Growth Rates Observed at Oregon, Barbados, Samoa, and Cape Grim. CCl_3F Data Are From the Porosil Column.

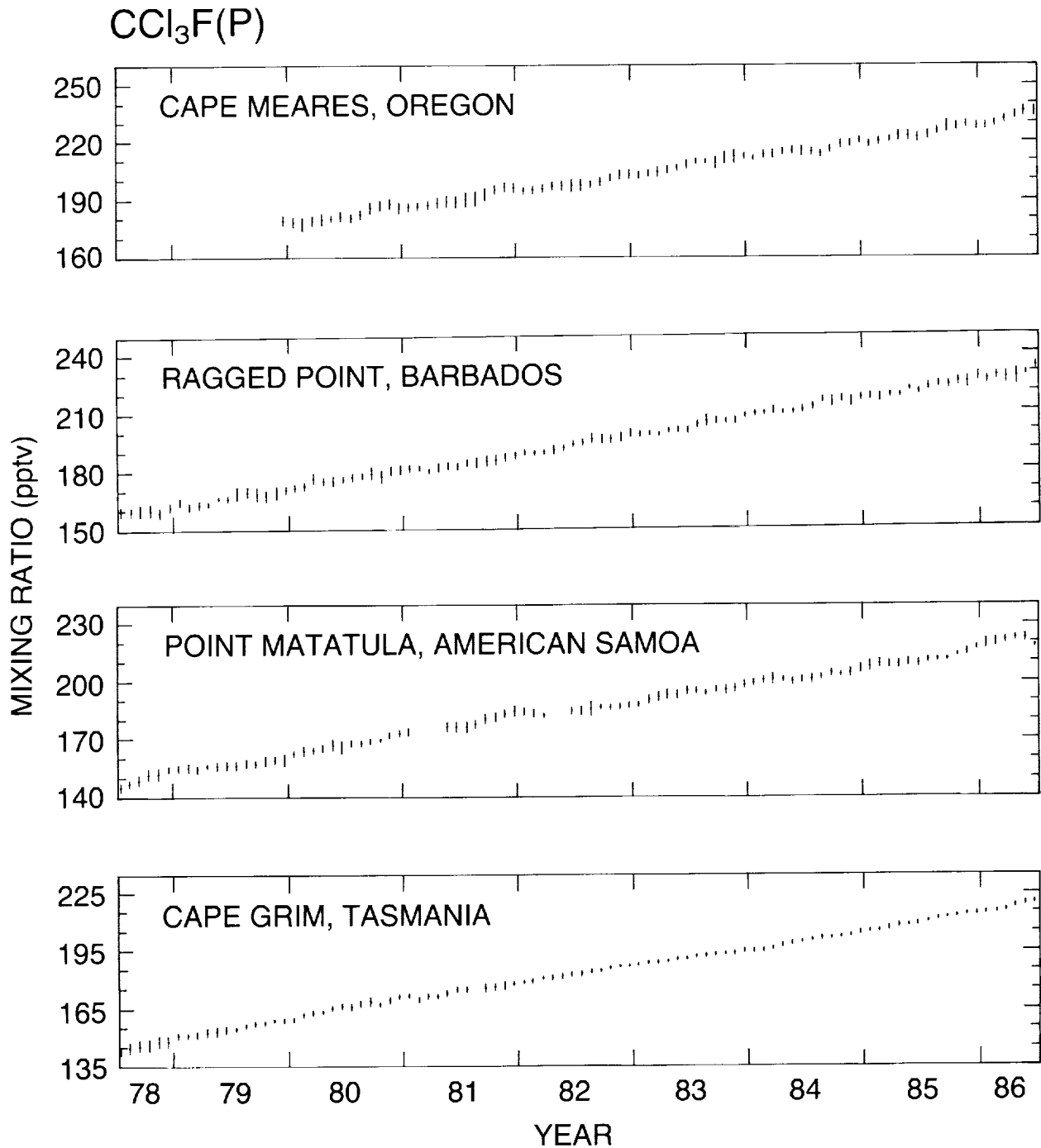|	CCl_3F	CCl_2F_2	CH_3CCl_3	CCl_4
Adrigole	8.6(0.1)	16.9(0.2)	6.9(0.2)	0.6(0.2)
Oregon	8.5(0.1)	16.6(0.2)	6.2(0.2)	1.4(0.1)
Barbados	9.2(0.1)	16.8(0.1)	6.3(0.1)	2.0(0.1)
Samoa	8.9(0.1)	16.6(0.1)	6.1(0.1)	1.9(0.1)
Cape Grim	9.2(0.1)	16.8(0.1)	6.3(0.1)	1.7(0.1)
Global Average	9.0(0.1)	16.7(0.1)	6.2(0.1)	1.8(0.3)

Figure 8.1 Monthly mean mixing ratios of CCl₃F measured with HP5840 and HP5880 gas chromatographs on porosil columns at the ALE–GAGE stations between July 1978 and June 1986 (see Prinn et al., 1983a; Rasmussen and Lovelock, 1983; Cunnold et al., 1983a; Cunnold et al., 1986, for further details). The data for 7/85 to 6/86 are preliminary (R. Prinn, R. Rasmussen, F. Alyea, D. Cunnold, A. Crawford, P. Fraser, P. Simmonds, and R. Rosen, private communication, 1987).
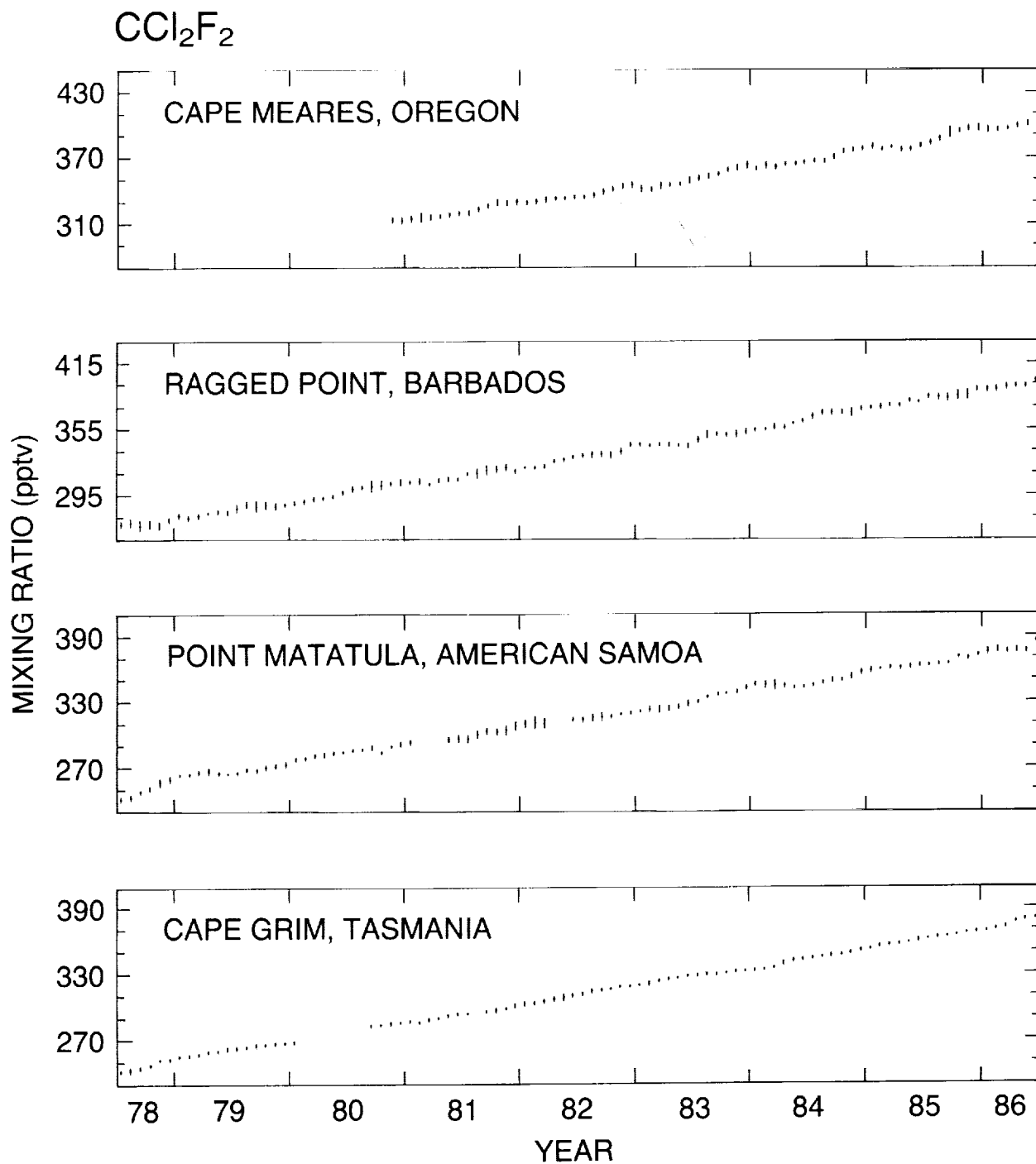
Figure 8.2 Monthly mean mixing ratios of CCl_2F_2 measured with HP5840 and HP5880 gas chromatographs on porosil columns at the ALE–GAGE stations between July 1978 and June 1986 (see Prinn et al., 1983a; Rasmussen and Lovelock, 1983; Cunnold et al., 1983b; Cunnold et al., 1986, for further details). The data for 7/85 to 6/86 are preliminary (R. Prinn, R. Rasmussen, F. Alyea, D. Cunnold, A. Crawford, P. Fraser, P. Simmonds, and R. Rosen, private communication, 1987).
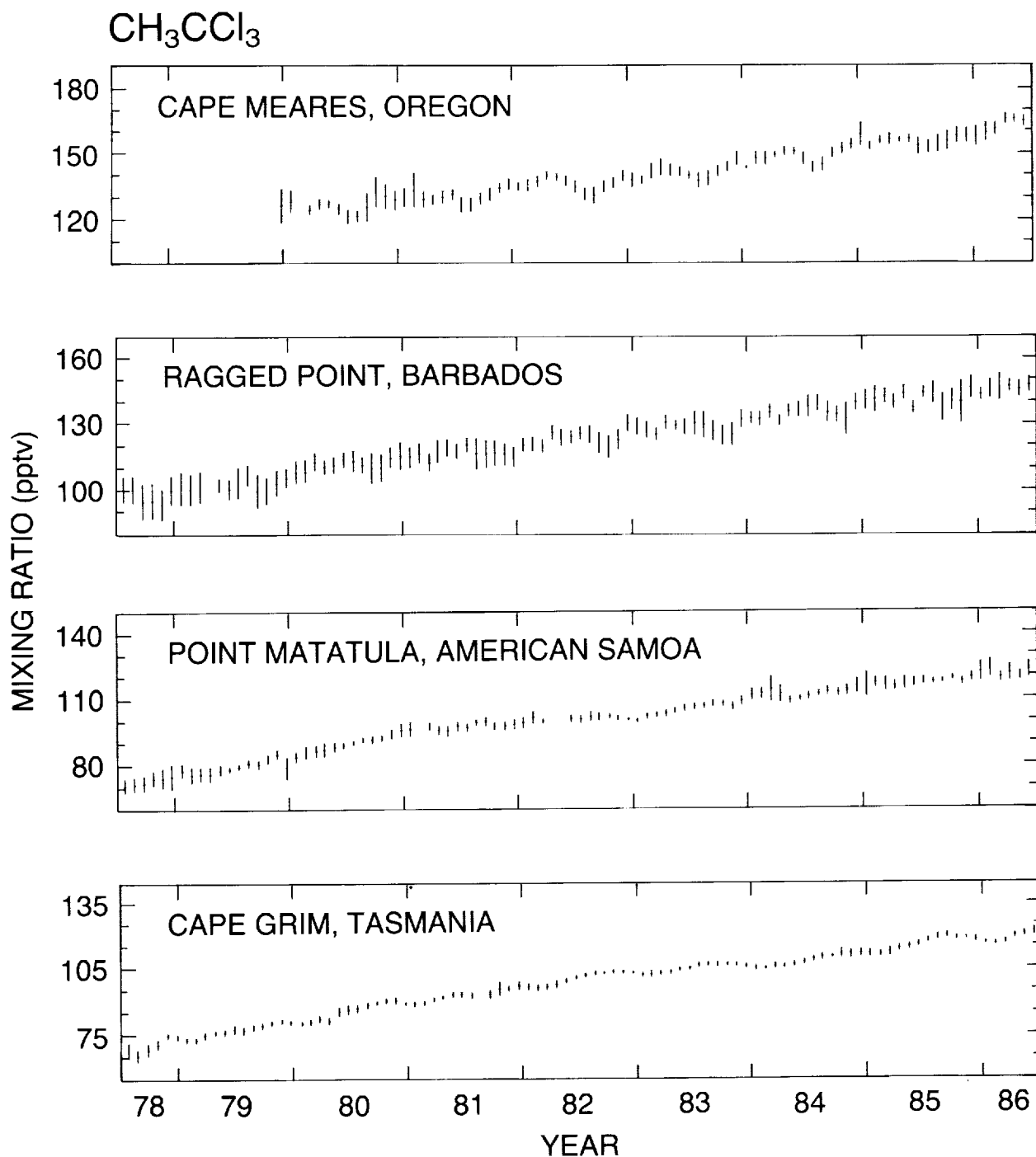
Figure 8.3 Monthly mean mixing ratios of CH₃CCl₃ measured with HP5840 and HP5880 gas chromatographs on silicone columns at the ALE–GAGE stations between July 1978 and June 1986 (see Prinn et al., 1983a; Rasmussen and Lovelock, 1983; Prinn et al., 1983b; Khalil and Rasmussen, 1984a; Prinn et al., 1987, for further details). The data for 7/85 to 6/86 are preliminary (R. Prinn, R. Rasmussen, F. Alyea, D. Cunnold, A. Crawford, P. Fraser, P. Simmonds, and R. Rosen, private communication, 1987).
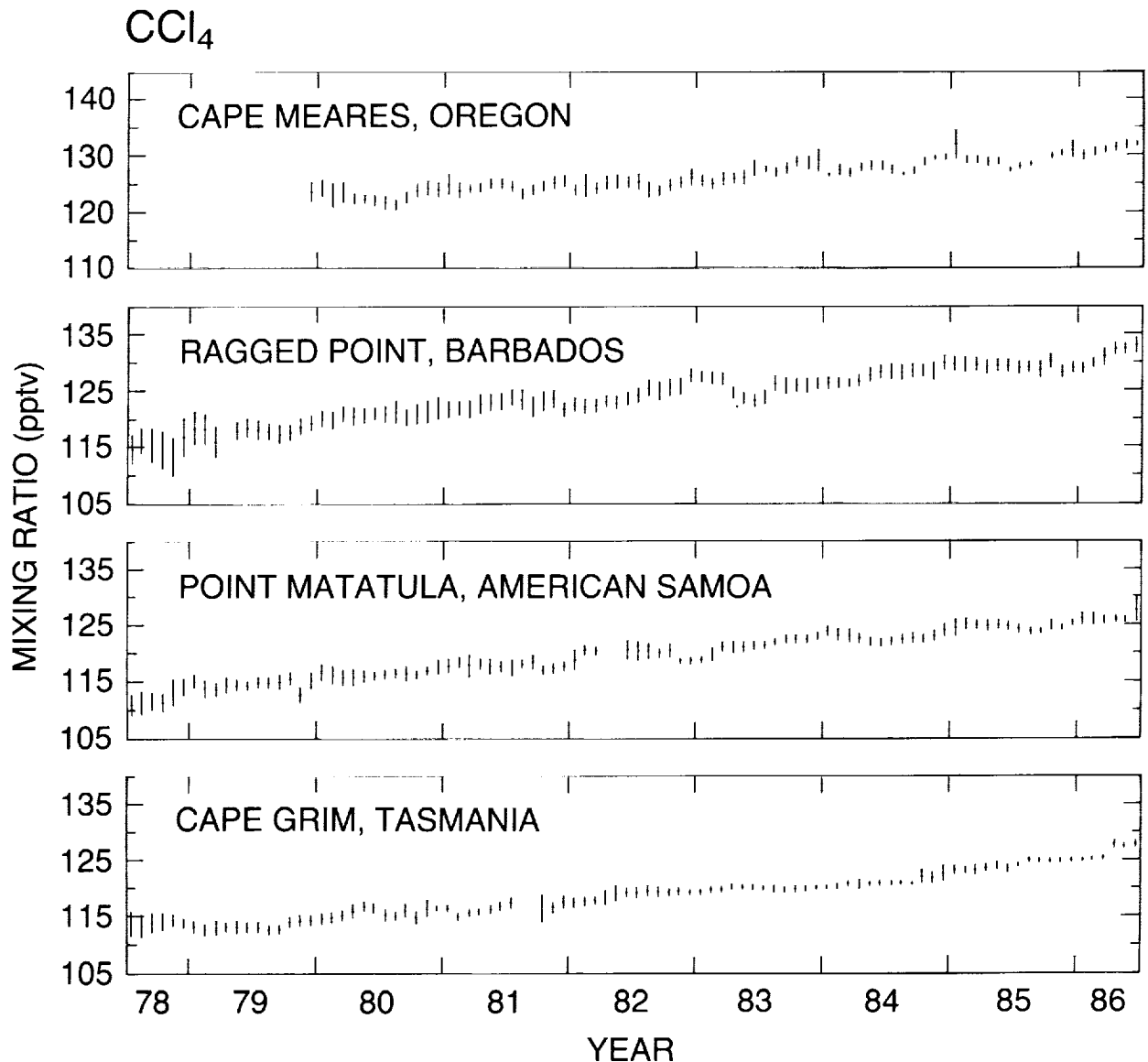
CCl$_4$

Figure 8.4 Monthly mean mixing ratios of CCl$_4$ measured with HP5840 and HP5880 gas chromatographs on silicone columns at the ALE–GAGE stations between July 1978 and June 1986 (see Prinn et al., 1983a; Rasmussen and Lovelock, 1983; Simmonds et al., 1983; Simmonds et al., 1986 for further details). The data for 7/85 to 6/86 are preliminary (R. Prinn, R. Rasmussen, F. Alyea, D. Cunnold, A. Crawford, P. Fraser, P. Simmonds, and R. Rosen, private communication, 1987).

for CCl$_2$F$_2$, 6.2(0.1) for CH$_3$CCl$_3$, and 1.8(0.3) for CCl$_4$. The numbers in parentheses are single standard deviations. Growth rates in 1985 averaged 4.2 percent per annum for CCl$_3$F, 4.5 percent for CCl$_2$F$_2$, 4.7 percent for CH$_3$CCl$_3$, and 1.4 percent for CCl$_4$ (Table 8.4).

One aim of ALE/GAGE is to determine the atmospheric lifetimes of these halocarbon gases, a key parameter controlling their ultimate impact on stratospheric chemistry and climate. The lifetimes are calculated by comparing independent estimates of release with the total amount or

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Table 8.4 Halocarbon Growth Rates (%/yr) Observed at the GAGE Sites in 1985. Data Are Obtained From Tables 8.1 and 8.2.

|	CCl_3F	CCl_2F_2	CH_3CCl_3	CCl_4
Oregon	3.8	4.3	4.0	1.1
Barbados	4.2	4.4	4.5	1.6
Samoa	4.2	4.6	5.2	1.5
Cape Grim	4.4	4.6	5.4	1.4
Global Average	4.2	4.5	4.7	1.4

rate of increase of these species in the atmospheres. Conversely, if independent lifetime calculations can be made, then the data can be inverted to derive releases. Since there are no new emission estimates of CCl_3F and CCl_2F_2 from industry, the measured global atmospheric increases of these species are an important way in the immediate future of monitoring the global release of these species. Results from the extended ALE–GAGE data set can be summarized as follows:

CCl_3F and CCl_2F_2

The lifetimes of CCl_3F and CCl_2F_2 are 74^{+31}_{-17} and 111^{+222}_{-44} years, respectively, from trend analysis of 5 years of data (1978 to 1983) (Cunnold et al., 1986). Both lifetimes are consistent with estimates of removal rates in the stratosphere. The uncertainties in the trend lifetime estimates are dominated by release uncertainties. Inverting the analysis, assuming stratospheric photo-dissociation to be the only atmospheric sink for CCl_3F and CCl_2F_2, yields annual release estimates with an accuracy that, based on the precision of the measurement system only, is claimed to be approximately 8 percent (Cunnold et al., 1986). The release estimate for CCl_3F derived from observations agrees with the Chemical Manufacturers Association estimate based on production (CMA, 1985); for CCl_2F_2, the estimate, although exhibiting variability from year to year, suggests that the emissions in the USSR and Eastern Europe have remained roughly constant over 1979 to 1982 at about 10 percent of global emissions (Cunnold et al., 1986).

CH_3CCl_3

Methylchloroform (CH_3CCl_3) is released to the atmosphere in larger amounts (500 to 550 × 10^6 kg per year) than any other anthropogenic chlorine-containing gas. Because it is susceptible to chemical attack by OH radicals.

$$CH_3CCl_3 + OH \rightarrow CH_2CCl_3 + H_2O,$$
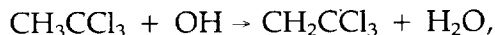
a larger fraction of CH_3CCl_3 molecules is removed in the troposphere, and its potential threat to stratospheric ozone depletion is correspondingly reduced.

The lifetime of CH_3CCl_3 was calculated to be $6.9^{+1.2}_{-0.9}$ years from trend analysis of 7 years of observations (1978 to 1985). A lifetime of $6.0^{+1.1}_{-0.8}$ years was obtained by comparing the total atmospheric content with the release data, and a third method, comparing observed and calculated latitudinal gradients, gave a lifetime of $6.0^{+1.4}_{-1.0}$ years. Combining all three ways of

analysing the CH_3CCl_3 data, the best estimate of the atmospheric lifetime of CH_3CCl_3 is $6.3^{+1.2}_{-0.9}$ years (Prinn et al., 1987). If 6.3 years is assumed to be the lifetime of CH_3CCl_3, then, by inverting the data, emissions can be calculated that generally agree with those deduced from industry data. The best estimate of a lifetime of 6.3 years corresponds to a globally averaged tropospheric OH concentration of $(7.7 \pm 1.4) \times 10^5 cm^{-3}$. This estimate is more accurate than that derived previously (Singh, 1977; Lovelock, 1977; Makide and Rowland, 1981; Prinn et al., 1983b; Khalil and Rasmussen, 1984a; Fraser et al., 1986a).

CCl_4

The observed trend and latitudinal gradient of CCl_4 are consistent with an atmospheric lifetime of about 40 years, and with releases of CCl_4 averaging $(9.0 \pm 0.9) \times 10^7 kg/year$ over the period 1978 to 1985. Consistency between release estimates and observations was obtained by assuming a CCl_4 calibration based on a comparison of ALE–GAGE data and the data collected by Makide et al. (1987a) on Hokkaido. The global release estimates suggest that the majority of CCl_4 is derived from chlorofluorocarbon production (Simmonds et al., 1986). However, on a regional scale, the observations at Adrigole, Ireland, imply that there is a significant contribution to European emissions from Eastern Europe, adding to the industrial losses and solvent use reported in Western Europe (Prather, 1985, 1988).

The data from Hokkaido obtained during 1985 are summarized in Table 8.5 and compared to similar GAGE data obtained at Cape Meares, Oregon. Concentrations of CCl_3F, CCl_2F_2, CH_3CCl_3, and CCl_4 on Hokkaido are 2 percent lower, 5 percent higher, 19 percent lower, and 18 percent lower, respectively, than those observed at Cape Meares. The concentration increases are similar at both locations for CCl_3F and CCl_2F_2 (4 to 5 percent per year), but significantly different for CH_3CCl_3, where a higher rate is observed in Oregon, and for CCl_4, where a higher rate is observed on Hokkaido. The differences in concentration for all species at both sites could be due largely to calibration differences. However, other factors such as the strength and location of regional sources and the different observation methodologies could contribute to the observed differences. The lower concentration of CCl_4 observed at Hokkaido has been used to support a lowering of the GAGE absolute calibration standard (Simmonds et al., 1986).

Table 8.5 Annual Mean Halocarbon Concentrations and Trends Observed at (a) Hokkaido, Japan (42° to 45°N) (Makide et al., 1987a), and (b) Oregon, USA (45°N) (GAGE data), in 1985. Concentrations Are in pptv, Annual Increases (pptv/yr) Were Obtained by Linear Regression, and the Number in Parentheses Is One Standard Deviation. Data at Both Sites Were Collected From 1979 to 1986.

	CCl_3F		CCl_2F_2		CH_3CCl_3		CCl_4	
	a	b	a	b	a	b	a	b
1985 Concentration	218.7	223.2	404.8	385.6	126.4	155.4	105.3	129.2
Increase (pptv/yr)	8.9 (0.3)	8.5 (0.1)	18.5 (0.6)	16.6 (0.2)	3.7 (0.4)	6.2 (0.2)	1.6 (0.5)	1.4 (0.1)
1985 Increase (%/yr)	4.1	3.8	4.6	4.3	2.9	4.0	1.5	1.1

Table 8.6 Annual Mean CCl$_3$F and CCl$_2$F$_2$ Concentrations (pptv) and Increases (pptv/yr, %/yr) Observed at the Five Geophysical Monitoring for Climatic Change Stations (GMCC, 1986a).

	CCl$_3$F	Increase		CCl$_2$F$_2$	Increase	
		pptv/yr	%/yr		pptv/yr	%/yr
Barrow	227.4	9.1(1.0)	4.0	390.7	15.8(0.1)	4.0
Niwot Ridge	223.7	9.1(1.0)	4.1	384.5	15.1(0.2)	3.9
Mauna Loa	220.5	9.4(0.1)	4.3	381.7	15.0(0.2)	3.9
Samoa	213.1	9.7(0.1)	4.6	374.3	16.9(0.1)	4.5
South Pole	216.3	9.6(0.4)	4.4	366.4	16.8(0.3)	4.6
Global Average	220.2	9.4	4.3	379.5	15.9	4.2

The GMCC data obtained in 1985 are summarized in Table 8.6. Globally averaged CCl$_3$F and CCl$_2$F$_2$ concentrations were both 1.7 percent higher than those observed in the GAGE program. At Samoa, where both programs share a common site, CCl$_3$F and CCl$_2$F$_2$ concentrations in 1985 were 1.0 and 3.1 percent higher, respectively. These differences could be due to calibration, but differences in sampling strategies and data rejection criteria to remove local pollution episodes might also contribute to a bias. The concentration increases observed globally are similar for both programs, 4.2 and 4.3 percent per year for CCl$_3$F from ALE–GAGE and GMCC programs, respectively, and, for CCl$_2$F$_2$, 4.2 percent per year by GMCC compared to 4.5 percent per year by GAGE.

8.3 OTHER CHLOROCARBONS

CCl$_2$FCClF$_2$ (CFC-113)

Observations of background concentrations of CCl$_2$FCClF$_2$ have been reviewed (*WMO*, 1986), but the data were not extensive enough to quantify global trends. Long time series of CCl$_2$FCClF$_2$ measurements have been made available based on the analysis of flask air samples collected in Alaska, Oregon, Hawaii, American Samoa, Tasmania, and at the South Pole (M.A.K. Khalil and R.A. Rasmussen, unpublished data), and in Hokkaido (Makide et al., 1987b).

The observed trends of CCl$_2$FCClF$_2$ are shown in Figure 8.5 as a global average of the six Khalil and Rasmussen sampling sites and for Hokkaido. For 1985, the average global concentration reported by Khalil and Rasmussen is approximately 31 pptv, whereas Makide et al. (1987b) deduce a 1985 average value on Hokkaido of 46 pptv. A large component of this discrepancy appears to be due to calibration differences; this needs to be resolved.

The annual increase in CCl$_2$FCClF$_2$ concentration based on linear regression is 3.6($\pm$0.1) pptv/yr or 11.6%/yr (1985) from the global average data (Khalil and Rasmussen), and 4.8($\pm$0.2) pptv/yr or 10.5%/yr (1985) from the Hokkaido data. The rate of increase could itself be increasing, since the last 4 years at Hokkaido show an increase of 11.6%/yr in 1985. The reasonable agreement between the two data sets for the %/yr increase (11 to 12 percent in 1985) supports the conclusion that the difference between the two data sets in absolute concentration is caused by a calibration problem.

The latitudinal distribution in 1985 for the six sampling sites of Khalil and Rasmussen is shown in Figure 8.6. The average concentration in the Southern Hemisphere is about 17 percent
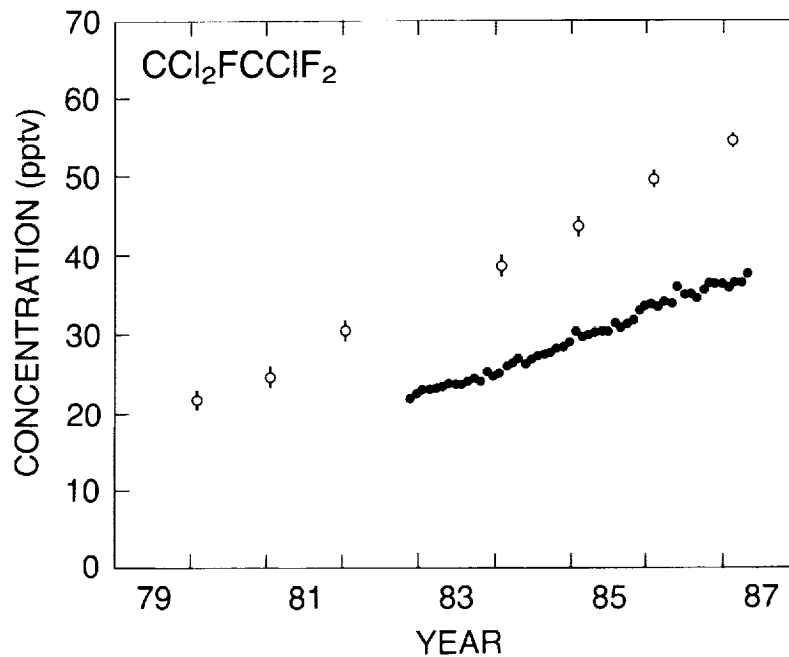
Figure 8.5 Trends of atmospheric concentrations of CCl₂FCClF₂ (CFC–113) observed in Hokkaido, Japan (43°–45°N; ○ Makide et al., 1987b), and as a global average of six sampling sites (76°N–90°S; ● M.A.K. Khalil and R.A. Rasmussen, unpublished data). Error bars are single standard deviations.
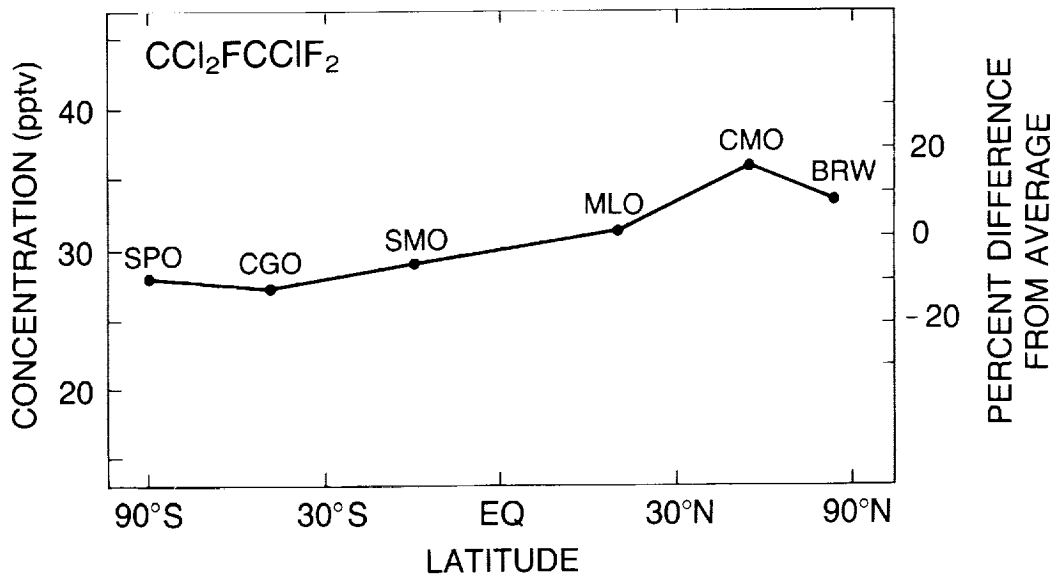

Figure 8.6 The global distribution of CCl₂FCClF₂ in 1985 from six sampling sites (BRW, Barrow, Alaska; CMO, Cape Meares, Oregon; MLO, Mauna Loa, Hawaii; SMO, Cape Matatula, American Samoa; CGO, Cape Grim, Tasmania; SPO, South Pole) (M.A.K. Khalil and R.A. Rasmussen, unpublished data).

lower than in the Northern Hemisphere, reflecting its dominant release in the Northern Hemisphere and rapid increase of atmospheric concentration.

$CHClF_2$ (CFC-22)

In the previous report (WMO, 1986) the only information available on the atmospheric trend of $CHClF_2$ was from an early paper of Khalil and Rasmussen (1981), which showed an increase of about 12%/yr. Unfortunately, very little further data are available. However, observations of $CHClF_2$ have been reported from Cape Grim, Tasmania (Khalil and Rasmussen, 1987a; Fraser et al., 1987a), which show an average 1985 concentration of 77 pptv increasing at 6.5 pptv/yr or 8.4%/yr. The data are shown in Figure 8.7. The global average concentration of $CHClF_2$, 92 pptv, given in Table 8.1, is based on the Cape Grim value and an interhemispheric concentration ratio of 1.16 (WMO, 1986).

CH_3Cl

Very little new information has appeared on CH_3Cl since the last report (WMO, 1986). Three years of observations at Cape Grim (Khalil and Rasmussen, 1987a; Fraser et al., 1987a) do not show any obvious change with time, apart from a clear annual cycle, which is presumably related to the removal of CH_3Cl from the atmosphere by hydroxyl radicals (Figure 8.8). A number of trace gases such as CH_3CCl_3, methane, and carbon monoxide at Cape Grim show annual cycles of phases similar to those observed for CH_3Cl, and they have been attributed to the seasonal variations in the magnitude of the hydroxyl radical sink (Fraser et al., 1986a). The global average concentration is approximately 600 pptv (see WMO, 1986).
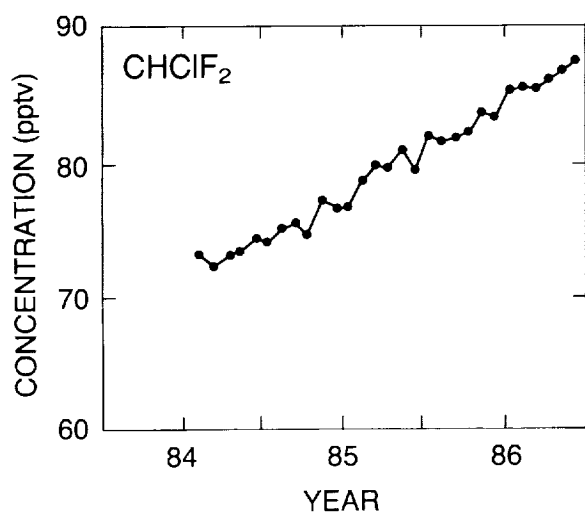

Figure 8.7 Monthly mean $CHClF_2$ observations (pptv) at Cape Grim, Tasmania, from the Oregon Graduate Center flask sampling program (Khalil and Rasmussen, 1987a; Fraser et al., 1987a).
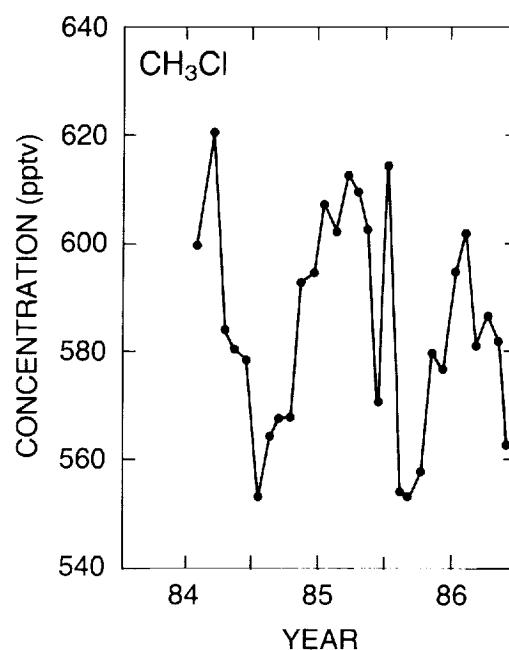
Figure 8.8 Monthly mean CH_3Cl observations (pptv) at Cape Grim, Tasmania, from the Oregon Graduate Center flask sampling program (Khalil and Rasmussen, 1987a; Fraser et al., 1987a).
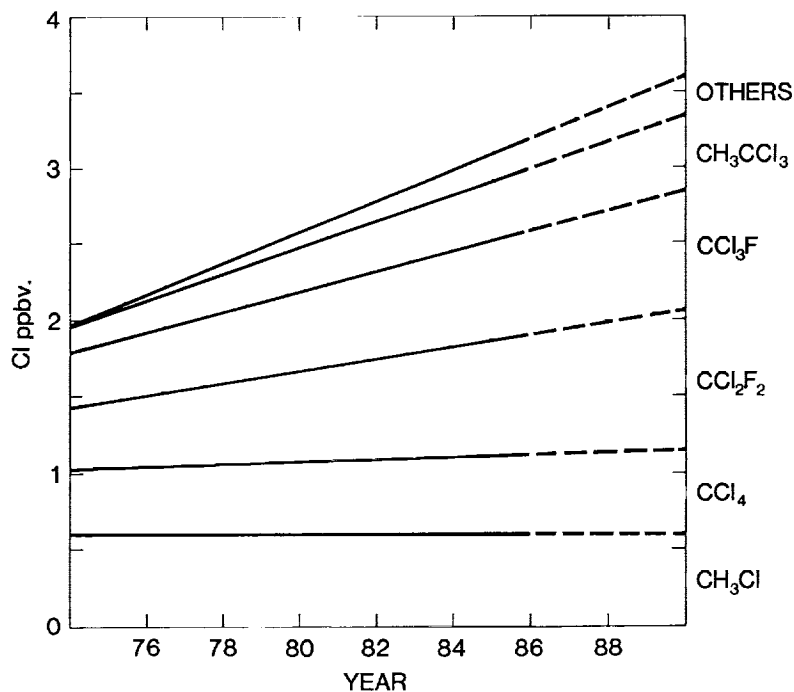
Figure 8.9 Measured and predicted cumulative increases of chlorinated source gases in the troposphere over the past decade and up to 1990. The concentrations are given as chlorine atom equivalents. Future increases are indicated by dashed lines, based on constant emission rates at current levels. CCl_3F, CCl_2F_2, CH_3CCL_3, CCl_4, and CCl_2FCClF_2 data are from the ALE–GAGE program (see Sections 8.2 and 8.3). $CHClF_2$ data are derived from Cape Grim data (see Section 8.3).

The largest perturbation in stratospheric ozone is expected from the observed increases in chlorinated source gases, which determine the growth of reactive chlorine species in the stratosphere. It is, therefore, instructive to look at the temporal increase of the total gaseous chlorine in the troposphere (Figure 8.9). The current rate of increase (1986) in total chlorine is 3.3 percent per year.

8.4 BROMOCARBON SPECIES

Interest in atmospheric bromine compounds has increased because of the possible role of bromine radicals in the loss of Antarctic ozone (McElroy et al., 1986a; Crutzen and Arnold, 1986; Isaksen and Stordal, 1986a). Relatively few studies have been made, however, and bromine compounds were considered only briefly in the previous report (WMO, 1986).

The last decade has seen the emergence of a new class of perhalogenated bromine gases, bromotrifluoromethane ($CBrF_3$, Halon–1301) and bromochlorodifluoromethane ($CBrClF_2$, Halon–1211). These chemicals are long lived in the atmosphere, and their use has been growing rapidly, particularly for fire suppression in military and high-technology environments. Concentrations in the upper troposphere and lower stratosphere were about 1 pptv for $CBrF_3$ in 1980 and 1.5 pptv for $CBrClF_2$ in 1984 (Fabian et al., 1981; Lal et al., 1985). Concentrations of both species appear to be increasing between 10 percent and 20 percent per year (Lal et al., 1985; Khalil and Rasmussen, 1985), and the total halon content in the Northern Hemisphere is now about 4.5
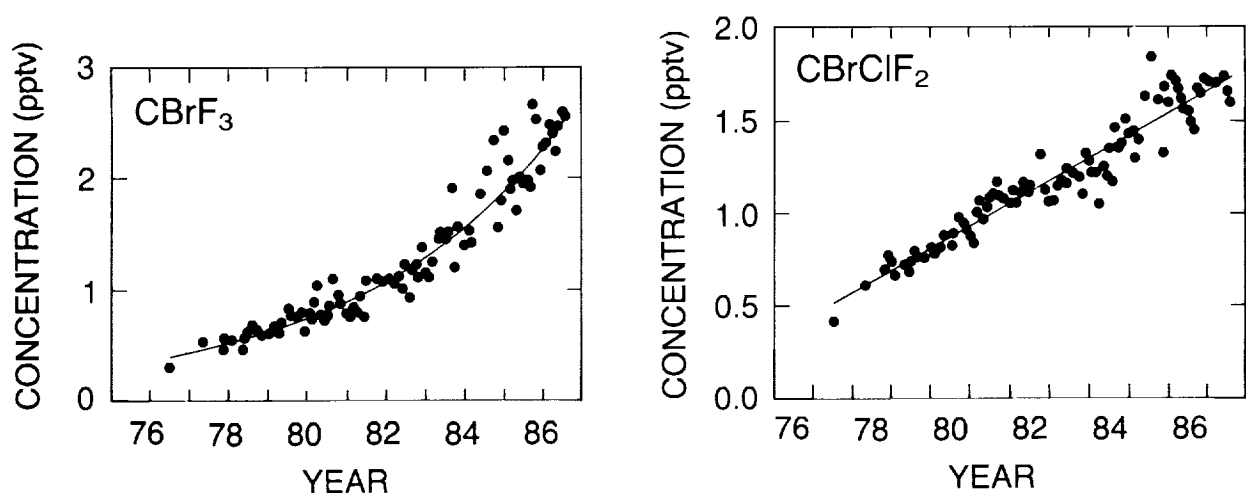
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Figure 8.10 Monthly mean concentrations of $CBrF_3$ and $CBrClF_2$ at Cape Meares, Oregon, over the last decade. Concentrations of $CBrF_3$ have increased exponentially at $18(\pm 1)$ percent/yr and linearly for $CBrClF_2$ at $0.12(\pm 0.01)$ pptv/yr (Khalil et al., 1986; R.A. Rasmussen, R. Gunawardena, and M.A.K. Khalil, unpublished data).

pptv (see Figure 8.10). The 1985 concentration of $CBrClF_2$ was 1.5 to 1.6 pptv at Cape Meares and about 1.3 to 1.5 at Cape Grim (see Figure 8.11). Although these results are based on data from only two stations, they should also apply globally, because the atmospheric lifetimes of the halons are quite long (see Table 8.1), so that these halons are well mixed globally. The rate of increase has accelerated dramatically since 1978, when concentrations were less than 0.5 pptv for each halon. The rate of increase of $CBrClF_2$ seems to be about 0.2 pptv/yr in both hemispheres. Stratospheric profiles indicate rapid decline with altitude above the tropopause, reflecting photolytic decomposition. The concentration at 20 km is less than 20 percent of the value at the tropopause (Fabian et al., 1981; Lal et al., 1985). Hence, there is little doubt that these compounds add significant quantities of bromine to the stratosphere.

New data and interpretations have emerged on organobromine gases of stratospheric importance, in addition to those for $CBrF_3$ and $CBrClF_2$. Salawitch et al. (1988a) have reviewed data on gaseous organic bromine from several investigators from the 1970's and 1980's. They note that major uncertainties, such as differences in experimental techniques, are involved, but they conclude that atmospheric CH_3Br has probably increased significantly, perhaps by a factor of two, in the past 10 years. Cicerone et al. (1988) have measured CH_3Br in almost 1,000 samples of air from five background sites, three in the Northern Hemisphere and two in the Southern Hemisphere, from January 1985 through September 1987. At all five sites, there were CH_3Br variations during this period, but trends are not yet clear. It appears that the current global background levels of CH_3Br are between 10 and 15 pptv (Salawitch et al., 1988a; Cicerone et al., 1988).

8.5 NITROUS OXIDE

Atmospheric nitrous oxide (N_2O) concentrations have continued to increase. R.F. Weiss (Scripps Institute of Oceanography) has extended the measurement program of Weiss (1981) into 1987. The results may be summarized as follows. Samples from over 1,100 flasks for the
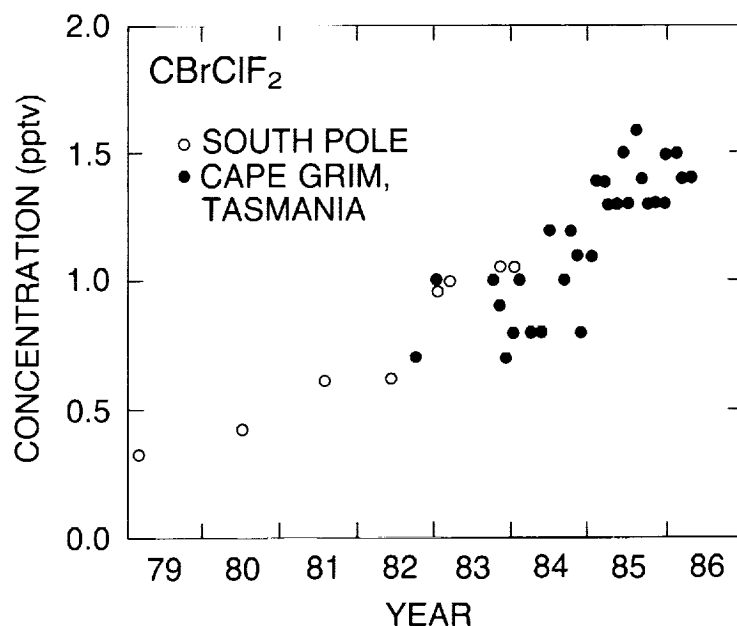
Figure 8.11 Observations of $CBrClF_2$ (pptv) in the Southern Hemisphere at Cape Grim, Tasmania (●), and at the South Pole (○) (Khalil and Rasmussen, 1985; Khalil et al., 1986; R.A. Rasmussen and R. Gunawardena, unpublished data).

period 1976 to early 1987 show very similar rates of N_2O increase. The January 1986 rates of increase are $0.65(\pm.02)$, $0.66(\pm.04)$, $0.67(\pm.04)$, and $0.61(\pm.04)$ ppbv/yr for all data, Barrow, Mauna Loa, and South Pole, respectively. The mean N_2O concentration in January 1986 was 304.8 ppbv. The complete data set, which includes flask samples from several ship tracks, displays a north–south gradient of $0.76(\pm.09)$ ppbv.

N_2O measurements have been made at the ALE–GAGE sites since July 1978 (Prinn et al., 1983a, 1988; WMO, 1986). Khalil (Oregon Graduate Center) has combined these data (about 60,000 real-time measurements) with flask measurements from Barrow and Mauna Loa (Khalil and Rasmussen, 1983a) to produce the global average shown in Figure 8.12. The average rate of increase of N_2O over the 7-year period 1979 to 1985 is $0.8(\pm0.05)$ ppbv/yr. The global average concentration in 1985 was 308.2 ppbv, with Northern Hemispheric concentrations being higher than Southern Hemispheric by $0.6(\pm0.1)$ ppbv.

N_2O measurements have been made on flasks collected at the GMCC sites since mid-1977 (GMCC, 1986a). J. Elkins (NOAA/GMCC) has analysed these data from 1978 through 1986; the rates of increase obtained by linear regression are $0.54(\pm0.06)$, $0.63(\pm0.09)$, $0.79(\pm0.07)$, $1.04(\pm0.08)$, and $0.57(\pm0.15)$ ppbv per year for Barrow, Niwot Ridge, Mauna Loa, Samoa, and the South Pole, respectively, the average rate being $0.7(\pm0.1)$ ppbv per year. The global average concentration in 1985 was 306.1 ppbv, with the three Northern Hemisphere stations being 2 ppbv higher than the South Pole. However, the GMCC observations at Samoa are approximately 6 ppbv higher than at the South Pole.

In summary, from three independent networks, the global rate of increase in N_2O ranges from 0.65 to 0.8 ppbv/yr, and the global average concentration ranges from approximately 305 to 308 ppbv, with the small differences probably due to differences in calibration.
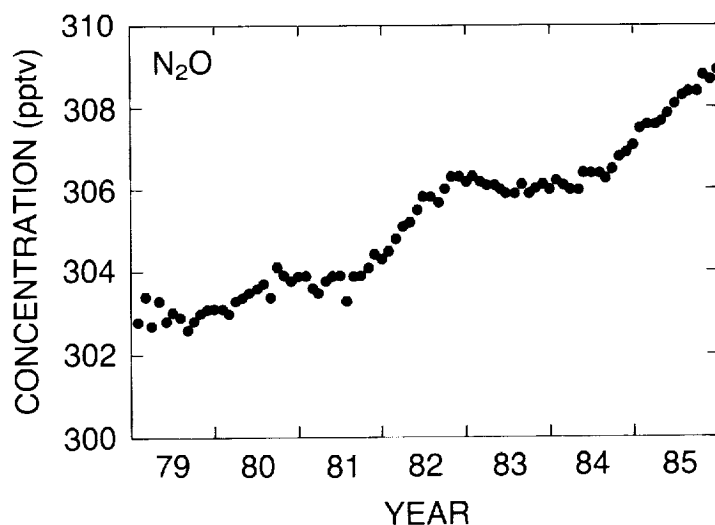
Figure 8.12 The monthly and globally averaged concentrations of N_2O based on ALE–GAGE data collected using in situ gas chromatographs at Adrigole, Cape Meares, Barbados, Samoa, and Cape Grim, and flask data from Barrow and Mauna Loa (Prinn et al., 1983a; Khalil and Rasmussen, 1983a; WMO, 1986; Prinn et al., 1988; M.A.K. Khalil and R.A. Rasmussen, unpublished data).

Evidence for a long-term trend in N_2O has been obtained from analysis of ice cores. Results from two recent studies are summarized in Figure 8.13 (Pearman et al., 1986; Khalil and Rasmussen, 1987b; Etheridge et al., 1987). The ice core data are noisy, but they do suggest that concentrations prior to 1800 were in the range of 280 to 290 ppbv. Measurements on modern ice (after 1960) are in reasonable agreement with current atmospheric observations.

Three possible sources of N_2O could account for the observed increases: (1) nitrification and denitrification of nitrogen from industrially produced nitrogenous fertilizers and wastes that are
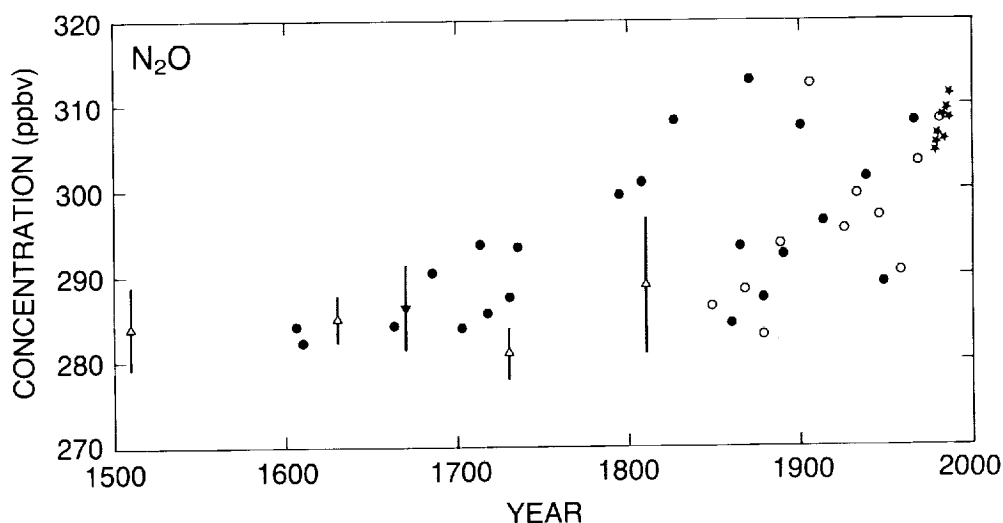

Figure 8.13 N_2O measurements obtained from ice cores. Data labeled ● and ○ are two different cores from Law Dome, Antarctica (Pearman et al., 1986; Etheridge et al., 1987; G.I. Pearman, D. Etheridge, F. de Silva, and P.J. Fraser, unpublished data); ▼ South Pole (Khalil and Rasmussen, 1987b) and △ Greenland (Khalil and Rasmussen, 1987b) with 90 percent confidence intervals. Data labeled ★ are in situ ALE–GAGE measurements from Cape Grim, Tasmania (Fraser et al., 1986b; Fraser and Derek, 1987).

attributable to this fertilizer, (2) biomass burning, and (3) high-temperature combustion (*WMO*, 1986). Evidence from Hao et al., 1987 shows that N_2O production in combustion is due largely to pre-existing nitrogen content of fuels (e.g., organic nitrogen in coals), and that this N_2O source can probably account for most of the observed N_2O increase. The reaction most likely to produce N_2O in this way is:

$$NO + NCO \rightarrow N_2O + CO \text{ (Perry, 1985)}.$$
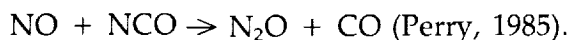
Very recent experiments by Muzio and Kramlich (1988) have demonstrated that the high-temperature combustion source of N_2O has been overestimated due to an unrecognized artifact in previous measurements. Thus, at present, our understanding of the causes of the contemporary N_2O increase is far from satisfactory.

8.6 METHANE

There are now four extensive data sets based upon direct measurements of atmospheric methane by gas chromatography with a flame ionization detector. These data sets have been generated by the Commonwealth Scientific and Industrial Research Organisation, Australia (CSIRO); the Geophysical Monitoring for Climatic Change (GMCC) program of the National Oceanic and Atmospheric Administration (NOAA); the Oregon Graduate Center, Beaverton, Oregon (OGC); and the University of California at Irvine (UC). The CSIRO program makes measurements at a number of sites, with the longest record being at Cape Grim. CSIRO also has made unique time series of measurements in the mid- and upper troposphere over the south-eastern Australian region by flask sampling from aircraft (Fraser et al., 1986a). The NOAA results are presented here as global average concentrations estimated from weekly flask sampling at over 20 sites in a globally distributed network (Steele et al., 1987). The OGC results are also global average values calculated as a weighted average of monthly mean concentrations from the six sites of Barrow, Cape Meares, Mauna Loa, Samoa, Cape Grim, and Antarctica (Khalil and Rasmussen, 1983b). The weighting factors for each site are determined according to the fraction of global surface area represented by each site (M.A.K. Khalil and R.A. Rasmussen, unpublished data). The UC data are also estimates of the global mean concentration based upon "snapshots" of the latitudinal profile from the Arctic to the mid-latitudes of the Southern Hemisphere, with appropriate weighting for latitude (Blake and Rowland, 1986 and 1988).

The CSIRO Cape Grim data, as well as the NOAA, OGC, and UC measurements, are shown in Figure 8.14, while the CSIRO mid-tropospheric data are shown in Figure 8.15. All methane concentrations are expressed in units of parts per billion by volume in dry air (ppbv). The CSIRO, NOAA, and OGC data are all based upon the same calibration scale (see Rasmussen and Khalil, 1981). The long-term increase is clearly evident in all data sets. Growth rates have been calculated as the slopes of least squares linear fits to the actual UC data, and to the 12-month running mean methane concentrations found from the other four data sets. To enable ready comparison of the growth rates from the different data records, the time period was restricted to be identical, or as close as possible, to that of the shortest record, namely, that of NOAA. These growth rates are given in Table 8.7. Over the 4-year period from April 1983 to May 1987, it is clear that the methane growth rate is less than 1 percent per year in all five data records. It is particularly significant that the CSIRO mid-tropospheric results give a growth rate identical to that found from the Cape Grim data, indicating that the long-term increase is indeed occurring throughout the atmosphere, and not just at surface locations. Contrary to previous reports, the long-term data (*WMO* 1986; Khalil and Rasmussen, 1986) do not show any significant effect due to the El Niño-Southern Oscillation.
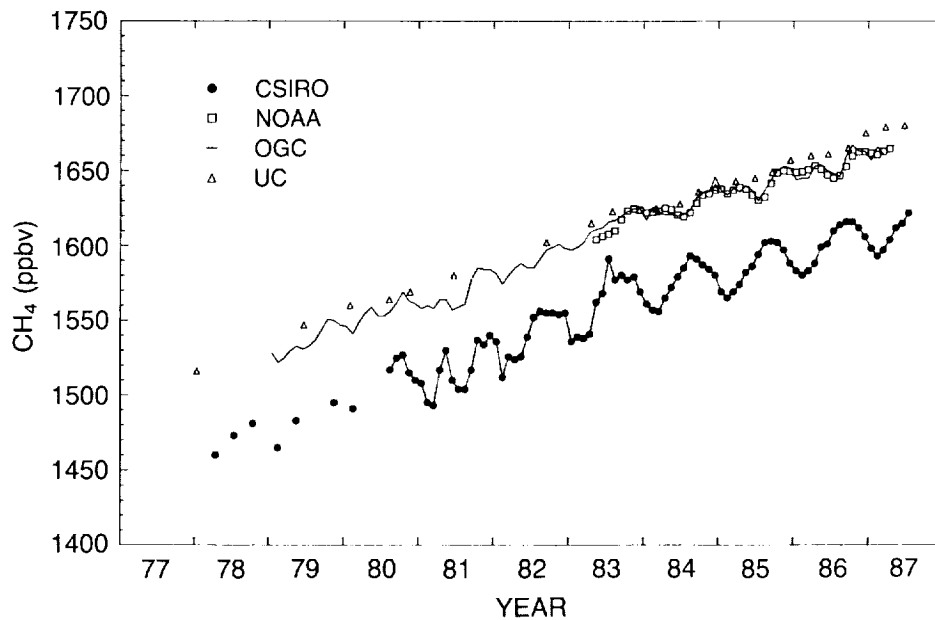
Figure 8.14 Results from four long-term, methane measurement programs based upon gas chromatography and flame ionization detection: (a) the Commonwealth Scientific and Industrial Research Organisation, Australia (CSIRO); (b) the Geophysical Monitoring for Climate Change program of the National Oceanic and Atmospheric Administration (NOAA); (c) the Institute of Atmospheric Sciences, Oregon Graduate Center (OGC); and (d) the University of California at Irvine (UC).

Data shown are monthly mean values except for UC (see text). For clarity, the monthly data of OGC are plotted as a solid line rather than as individual points. All values are estimates of the global average concentration except for those of CSIRO, which are for Cape Grim, Tasmania. The lower values for the CSIRO data set reflect the observed latitudinal gradient in methane concentrations.
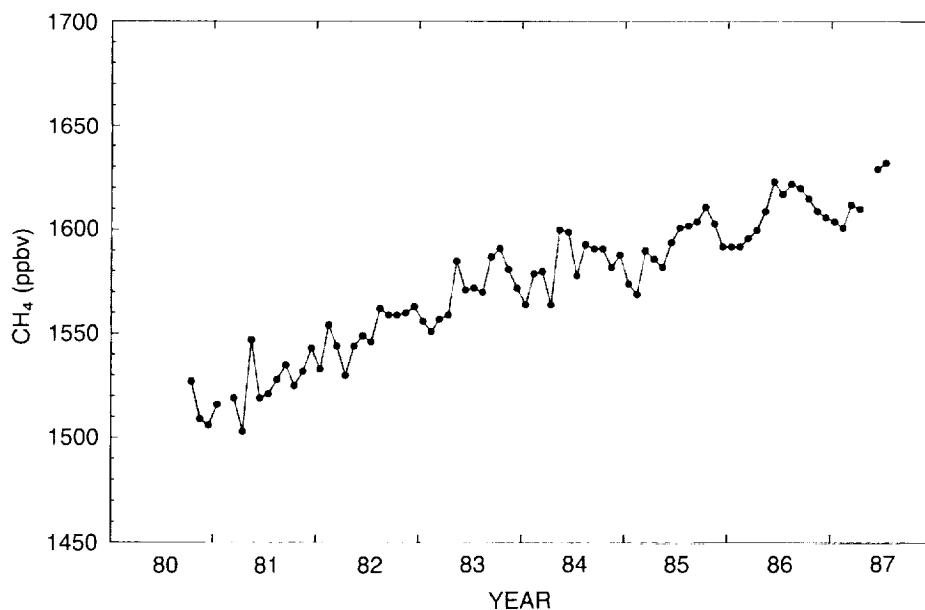

Figure 8.15 Time series of monthly mean methane concentrations measured by flask sampling from aircraft in the mid-troposphere (3.5 to 5.5 km altitude) over the southeastern Australian region (Fraser et al., 1986a, and unpublished data of P.J. Fraser et al.).

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Table 8.7 Comparison of Growth Rates of Atmospheric Methane. For All Data Sets Except UC the Growth Rates Are Given by the Slope of a Least Squares Linear Fit to 12-Month Running Mean Methane Values Calculated From the Monthly Data. The Values in Parentheses Are the Standard Errors of These Slopes. The Growth Rate for the UC Data Was Found by a Least Squares Linear Fit to the Actual Data Over the Period Specified.

Program	CH_4 Growth Rate (ppbv/yr)	Period Covered
CSIRO, Cape Grim	11.9(0.2)	May 83 – Apr 87
NOAA/GMCC (global)	12.92(0.04)	May 83 – Apr 87
OGC (global)	13.1(0.1)	May 83 – Mar 87
UC (global)	15.8(0.6)	Apr 83 – Mar 87
CSIRO, mid-troposphere (Southern Hemisphere)	11.9(0.9)	May 83 – Apr 87

Recently, the solar infrared spectra taken from Jungfraujoch in 1951 were evaluated, and an annual average column density of methane was obtained (Zander et al., 1989). In addition, new measurements at Jungfraujoch in 1985 and 1986 show a well-defined seasonal variation in the total methane column density. Comparison of these annual average column densities for 1951 and 1985 to 1986 indicates an average increase of .72 ($\pm$.15)%/yr over this period (Zander et al., 1989; cf. Ehhalt et al., 1983). This rate of increase is significantly lower than the value of 1.1($\pm$0.2)%/yr reported by Rinsland et al. (1985), who used a less complete set of the 1951 solar infrared spectra from Jungfraujoch.

The zonally averaged distribution of methane in the remote marine boundary layer is shown in Figure 8.16. This figure shows 4 years of results from the NOAA/GMCC cooperative flask
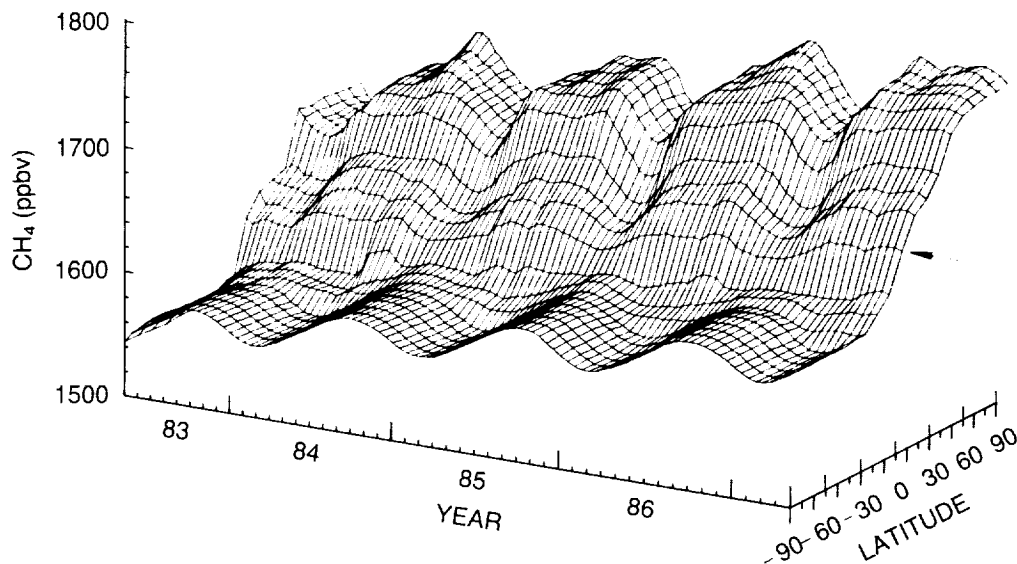

Figure 8.16 Zonally averaged representation of the variations in atmospheric methane concentrations in the remote marine boundary layer for the 4-year period May 1983 to April 1987. Grid spacing is 10° in latitude, and 0.5 month in time. The arrow indicates the position of the Equator. Data used to construct this figure are drawn from the globally distributed cooperative flask sampling network of NOAA/GMCC (Steele et al., 1987, and unpublished data of L.P. Steele).

sampling network, which now comprises 26 globally distributed sites (Steele et al., 1987, and unpublished results of L.P. Steele et al.). The seasonality in the Southern Hemisphere is quite repeatable from one year to the next, but less so in the Northern Hemisphere. Nevertheless, over this period the annually averaged latitudinal gradient of methane has not changed.

Many studies have reported the measurement of methane concentrations in air bubbles trapped in ice from both Antarctica and Greenland (Robbins et al., 1973; Craig and Chou, 1982; Khalil and Rasmussen, 1982; Rasmussen and Khalil, 1984; Stauffer et al., 1985; Pearman et al., 1986; Etheridge et al., 1987). If these air bubbles are truly indicative of atmospheric methane levels at the time that they were trapped in the ice, then the results from all of these studies (see Figure 8.17) are broadly consistent and show that, over the past 300 years, there has been more than a doubling of methane concentrations.

8.7 TRACE GASES INFLUENCING TROPOSPHERIC OZONE AND HYDROXYL RADICAL CONCENTRATIONS

A number of reactive trace gases play an important role in tropospheric chemistry because they influence the tropospheric distribution of ozone and hydroxyl radicals. Methane, carbon monoxide, and the nitrogen oxides are examples. All of these have strong anthropogenic sources and thus are expected to increase on a global or at least on a hemispheric scale. The trend in troposphere CH_4 was discussed above. Evidence for possible increases in CO and NO_x is described in the following paragraphs.

Carbon Monoxide

Since about half of the atmospheric CO is estimated to come from anthropogenic activities, primarily from combustion sources and from the oxidation of methane, it is expected that the
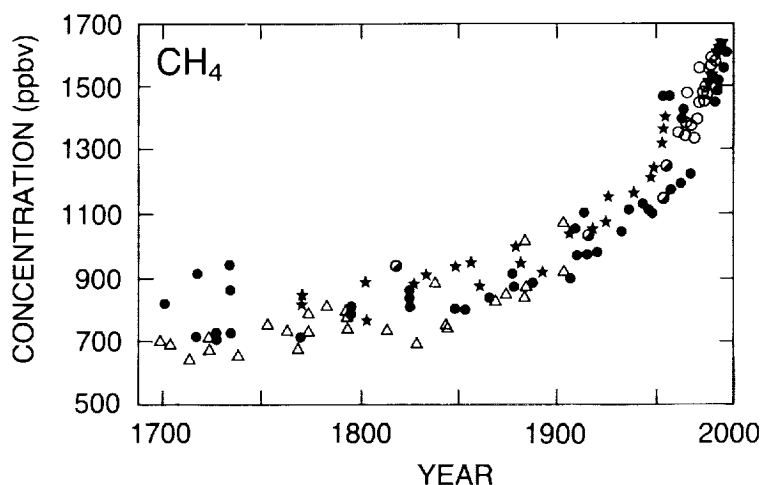

Figure 8.17 Summary of methane concentrations measured in air bubbles extracted from ice cores in both Greenland and Antarctica. Data are from several investigations, and differing methods of extracting the air from the ice have been used. References: ★, Stauffer et al. (1985); △, Khalil and Rasmussen (1982), Rasmussen and Khalil (1984); ○, Craig and Chou (1982); ●, Pearman et al. (1986), Etheridge et al. (1987), G.I. Pearman, D. Etheridge, F. de Silva, and P.J. Fraser, unpublished data. ▼ and ○ are globally averaged methane concentrations obtained from recent (Rasmussen and Khalil, 1986) and early (Khalil and Rasmussen, 1987c) gas chromatographic measurements of ambient air, respectively.

concentration of CO should increase as these sources continue to grow. However, because of short residence time (2 to 3 months), the determination of a secular trend in CO concentrations is very difficult.

The evidence for a global increase of CO has been controversial. A number of studies have estimated local CO trends ranging from 0 to 6 percent per year (Graedel and McRae, 1980; Dianov-Klokov and Yurganov, 1981; Dvoryashina et al., 1984; Seiler et al., 1984; Khalil and Rasmussen, 1984b; Rinsland and Levine, 1985; Fraser et al., 1986a,c). From these data, it would appear that CO concentrations in the Northern Hemisphere have increased in the past 15 to 30 years, but there is no convincing evidence of a Southern Hemisphere trend (Cicerone, 1988).

Recent analyses of measurements spanning 6 to 8 years suggest a global trend of about $1.0(\pm 0.4)\%/yr$ (Khalil and Rasmussen, 1988). The measurement sites are those of the Oregon Graduate Center flask sampling network, as well as the Cape Meares station, which incorporates in situ measurements, and Barrow, Mauna Loa and Cape Kumukahi (Hawaii), Samoa, Tasmania, and the South Pole. In Figure 8.18, the Northern Hemispheric, Southern Hemispheric, and global average concentrations are shown as monthly averages. The trends are claimed to be significant at the 95 percent level. At most individual sites, the trends are positive, but significantly greater than 0 only at the 90 percent level. At Cape Grim, the trend is very small and not statistically significant. It should be noted, however, that the estimation of a secular trend for CO is particularly difficult, because the species is short lived and shows a strong seasonal and spatial variation. Overcoming these problems requires long data records at a sufficiently large number of stations and a careful deseasonalization of the data. It is not clear that all these requirements are met by the available data sets.
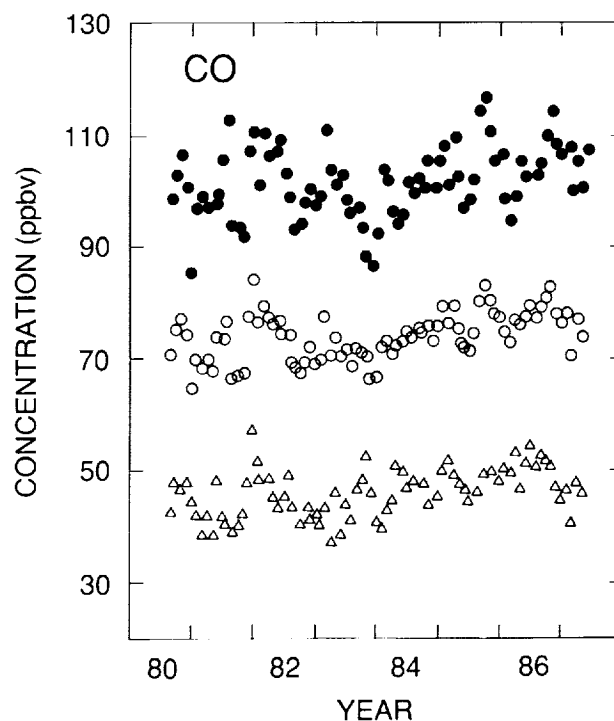

Figure 8.18 Hemispheric (●, Northern Hemisphere; Δ, Southern Hemisphere) and global (○) averages of deseasonalized CO concentrations (M.A.K. Khalil and R.A. Rasmussen, unpublished data).

Data from another flask sampling network in the Southern Hemisphere (Samoa; Cape Grim, Tasmania; Mawson, Antarctica; the South Pole; and the middle and upper troposphere over southeast Australia) do not show evidence for increasing concentrations of CO (Fraser et al., 1986a,c; Fraser et al., 1987b). The surface data are summarized in Figure 8.19.

In summary, it would appear that atmospheric CO concentrations have increased in the Northern Hemisphere, but, if they have increased in the Southern Hemisphere, the trend is probably smaller than the limit of detection of the current observational networks.

Nitrogen Oxides

Atmospheric nitrogen oxides (NO_x) are eventually converted to nitric acid, HNO_3, or aerosol nitrate, NO_3^-, and deposited at the Earth's surface. It has been proposed to use the measurement of NO_3^- in ice cores as an indicator of NO_x concentrations in the past atmosphere. Under present climatic conditions, nitrate is present in polar ice mainly as nitric acid (Legrand and Delmas, 1984). From measurements along an ice core collected in Greenland covering the last 100 years (Figure 8.20, curve A), Neftel et al. (1985) found a significant increase in NO_3^- that suggested that the NO_x budget of the high latitudes in the Northern Hemisphere has been significantly modified by human activities. In contrast, the nitrate profile observed in Antarctica over the same time period (Figure 8.20, curve B) exhibits no such trend, suggesting that the influence of anthropogenic NO_x was limited to the Northern Hemisphere. However, it currently is not possible to translate the observed NO_3^- increase in Greenland ice into a more quantitative statement about the NO_x budget of the Northern Hemisphere. The nitrate profiles from the South Pole do not support an earlier suggestion by Laird (1983) and Dreschhoff et al. (1983) of a modulation in NO_3^- deposition by solar activity (Herron, 1982; Legrand and Delmas, 1986).
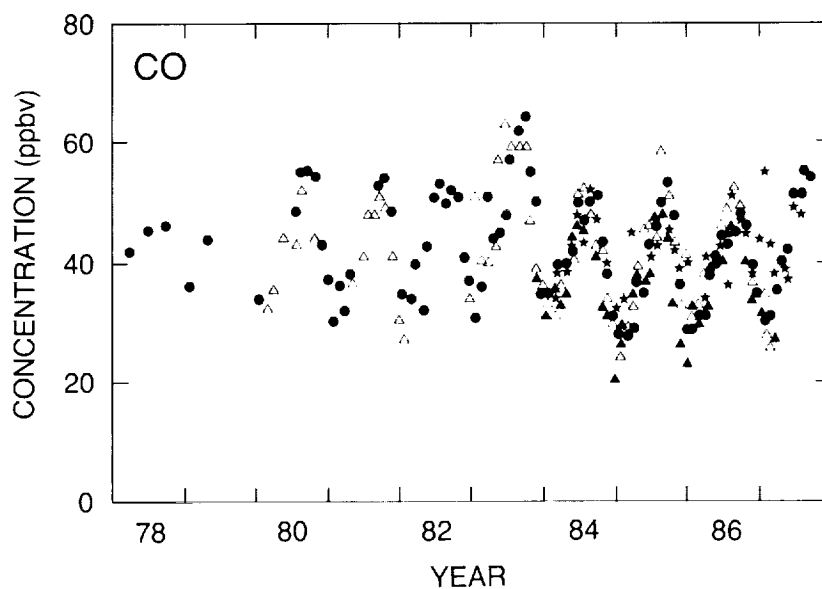

Figure 8.19 Monthly mean CO observations in the Southern Hemisphere from Samoa (★), Cape Grim (●), Mawson (△), and the South Pole (▲) (Fraser et al., 1986a,c; Fraser et al., 1987b; P.J. Fraser, unpublished data).
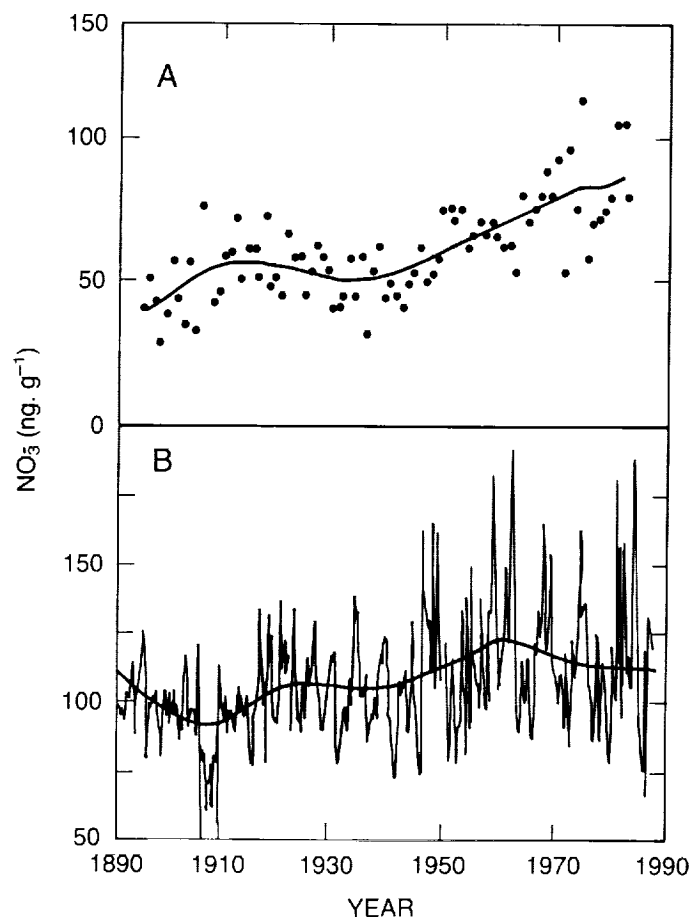
Figure 8.20 Nitrate (NO_3^-) trends over the last 100 years: (a) Dye 3, South Queensland (Neftel et al., 1985). (b) South Pole, Antarctica (S. Kircher, personal communication).

Carbon Dioxide

Carbon dioxide is not a photochemically active species in either the troposphere or the stratosphere. However, it is included in a discussion of source gases because it has a strong influence on the temperature-dependent photochemistry of the stratosphere, and, for example, it can thus influence levels and trends of stratospheric ozone.

While the long-term global rate of increase is about 1.5 ppmv per year (Fraser et al., 1983), the growth rate during 1981 to 1985 has been significantly lower, at approximately 1.2 ppmv per year. This lower growth rate is due, at least in part, to the effect of the intense ENSO event during 1982 to 1983 (see Conway et al., 1988; GMCC, 1986b).

8.8 CONCLUSIONS

Many of the source gases show a significant and well-documented increase in tropospheric concentration. The current rates of increase, along with the current concentrations and estimates of tropospheric lifetimes, are summarized in Table 8.1.

Available evidence indicates that increases in the atmospheric levels of CH_4, CO_2, and N_2O have been sustaining for long periods and that the increases derive from large-scale human activities, mainly food and energy production. From this viewpoint, it would be expected that possible trends in CO and NO_x may also have been sustained for a long time. It also seems improbable that the present trends of these gases will be arrested or reversed in the near future.

The highest relative rates of increase are observed for the exclusively manmade source gases (all gases in Table 8.1 except CH_3Cl, CH_3Br, N_2O, CH_4, and CO_2), because their lifetimes are long compared to the time since the beginning of release and they have not reached steady state. The two exceptions are CCl_4 and CH_3CCl_3, which are approaching steady state. The manmade halogen-containing gases are expected to continue their increase in the immediate future.

Evidence for increasing concentrations of $CBrClF_2$ and $CBrF_3$, often referred to as halons, is only just beginning to become available. Together with CH_3Br, they cause the total concentration of bromine to increase in the troposphere.

It is noted that the absolute accuracy of the concentration measurement is still unsatisfactory for some source gases, e.g., CCl_4, CH_3Br, $CBrClF_2$, $CBrF_3$, CCL_2FCClF_2, $CHClF_2$, and CO—mainly because calibration standards of suitable concentrations and integrity are not available. In addition, the global rates of increase for most of these gases are uncertain: for $CHClF_2$, $CBrClF_2$, and $CBrF_3$ because their increase has been monitored at only a few stations. Nevertheless, for the latter gases, the lifetimes are sufficiently long such that local increases are indicative of a global trend. The existence of a global trend in atmospheric CO levels remains uncertain.