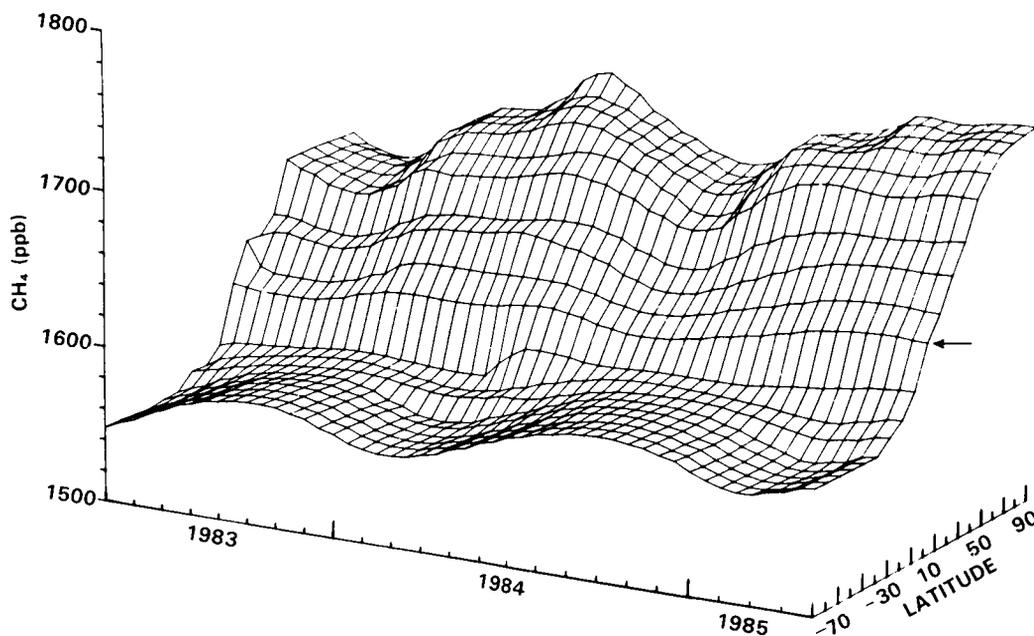


TROPOSPHERIC TRACE GASES



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CHAPTER 3

TROPOSPHERIC TRACE GASES: SOURCES, DISTRIBUTIONS AND TRENDS

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3.0 INTRODUCTION

Trace gases released at the earth's surface into the lower atmosphere influence the chemistry of the stratosphere in several ways. Some tropospheric trace species participate directly in the ozone photochemistry in the stratosphere. Such gases as N_2O and the halocarbons are sufficiently long-lived and insoluble to reach the stratosphere. There they are destroyed by photochemical reactions which generate free radical products (e.g. NO , Cl , Br), and these enter into the catalytic cycles which control ozone abundance.

Water vapor is directly involved in the odd-hydrogen and odd oxygen chemical cycles in the stratosphere. Most of the water vapor in the troposphere is trapped at the temperature minimum which separates the troposphere from the stratosphere. The low water vapor content of the stratosphere (a few ppm) is controlled by freezing out processes at the tropical tropopause and by stratosphere-troposphere exchange processes. Oxidation of CH_4 provides an important source of stratospheric H_2O which bypasses the cold trap. Another important role of CH_4 in stratospheric chemistry termination of chlorine radical chain reactions, via $(\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3)$.

Trace gases may affect stratospheric chemistry indirectly by influencing the delivery of reactive species to the stratosphere, for example, by altering the tropospheric lifetime for a key species such as CH_4 . In this sense, any tropospheric trace gas which significantly affects the photochemistry of the free troposphere (e.g., by altering local OH) indirectly affects the chemical balance in the stratosphere. Carbon monoxide, methane, oxides of nitrogen and other hydrocarbons all influence global tropospheric OH , and hence the major gas-phase scavenging process of the lower atmosphere.

There are several important species which influence stratospheric chemistry by altering the local physical conditions (temperature, insolation) in the stratosphere. For example, the "greenhouse" gases (CO_2 , H_2O , etc.) will affect stratospheric temperature, and hence temperature-dependent photochemical reaction rates. The trace gas carbonyl sulfide is a major gaseous source for the natural stratospheric sulfate aerosol layer.

Trace gas concentrations in the atmosphere reflect in part the overall metabolism of the biosphere, and in part the broad range of human activities such as agriculture, production of industrial chemicals, and combustion of fossil fuels and biomass. There is compelling evidence that the composition of the atmosphere is now changing, due to increased gaseous emissions associated at least in part with human activities. Observed trends in trace gas levels are reviewed and implications for the chemistry of the atmosphere are discussed in this chapter, with emphasis on those species influencing stratospheric chemistry and climate.

Species have been ordered in this discussion, beginning with gases derived from purely human sources and proceeding to those with both anthropogenic and natural sources. There are four principal classes of compounds for which emissions are affected by human activities: industrially manufactured gases (e.g. fluorocarbons), gases released in the production and consumption of fossil carbon fuels (CO_2 , CO , N_2O , oxides of nitrogen), gases arising from biomass burning (CH_3Cl , OCS , NO_x , N_2O , CO_2 , CO), and finally, biogenic gases released from agricultural lands, from soils or plants disturbed by development or exploitation, or from decomposing human or animal wastes. Throughout the discussion, particular emphasis is given to those species which are now increasing in the atmosphere, with a view towards understanding the causes of these important trends.

SOURCE GASES

3.1 HALOCARBONS

3.1.1 Distributions and Trends

Global baseline measurements of halocarbons CFC-11 (CFCl_3), CFC-12 (CF_2Cl_2), CCl_4 and CH_3CCl_3 were undertaken by the Atmospheric Lifetime Experiment, ("ALE", Prinn *et al.*, 1983a) beginning in 1978 and continuing to the present (now called the GAGE program). This study provided accurate descriptions of global distributions and trends for these key species, using careful calibration and intercomparison procedures to obtain self-consistent, absolute measurements at five coastal or island stations generally sampling unpolluted maritime air.

Figures 3-1 to 3-5 show results for these species (as monthly means) through June 1984 (Cunnold *et al.*, 1983a,b; Prinn *et al.*, 1983b; Simmonds *et al.*, 1983; all results are updated through 1984). The concentration for each gas is increasing with time, with growth rates averaging 5% per annum for CFC-11 and CFC-12, about 7% per annum for CH_3CCl_3 , and 1% per annum for CCl_4 . Concentrations of all species were observed to be higher in the Northern Hemisphere than in the Southern Hemisphere. Rates of increase, however, were larger in the Southern Hemisphere, indicating systematic gradual decline in the North-South asymmetry. The large excess of halocarbon concentrations in the North may be attributed to the dominant role of emissions from northern industrial areas and to the fact that the global distribution is far from a steady state. The decline of the North/South asymmetry reflects the slower growth rates for Northern emissions since the mid-1970's and increased importance for emissions in the Southern Hemisphere (see below).

One purpose of the ALE investigation was to determine the atmospheric lifetime for each gas, a key parameter controlling the ultimate impact of the gas on stratospheric chemistry. The largest uncertainties in analyzing lifetimes are associated with estimates of emission magnitude and/or estimates of the history of emission rates. The ALE investigators used two methods to assess lifetimes, one based on the atmospheric burden and on absolute source strength, the other based on the slope of the trend line and on the time history of emissions. Results using the extended data set (ALE + GAGE) may be summarized as follows (Prinn, Cunnold, Alyea, Rasmussen, Simmonds, Fraser, Crawford and Rosen, private communication, 1985):

CFC-11: The lifetime of CFCl_3 is 75^{+32}_{-17} years from the ALE trend analysis, consistent with estimates of removal rates in the stratosphere. It is unlikely that there is another globally significant removal process for this gas (Cunnold *et al.*, 1983a).

CFC-12: The trend lifetime estimate is 111^{+289}_{-46} years, again consistent with removal only in the stratosphere. There is greater uncertainty in this case than for CFC-11, due to inadequate knowledge of release rates (see below) (Cunnold *et al.*, 1983b).

CH_3CCl_3 : Using the currently accepted calibration, the lifetime of this species is estimated using the inventory technique to be 6.5^{+3}_{-2} years, in agreement with recent estimates by Khalil and Rasmussen (1984a). The inventory technique is strongly dependent on absolute calibration and very sensitive to estimated global emissions, both of which could be in error. Indeed, a change of 25% in either quantity could change the estimated lifetime by a factor of 2 (Logan *et al.*, 1981). For comparison, the lifetime estimate for trend analysis is 8.9 years. The major removal mechanism is almost certainly reaction with tropospheric OH. Current models for tropospheric photochemistry appear to give removal rates very close to the range given by the ALE analysis (Prinn *et al.*, 1983b).

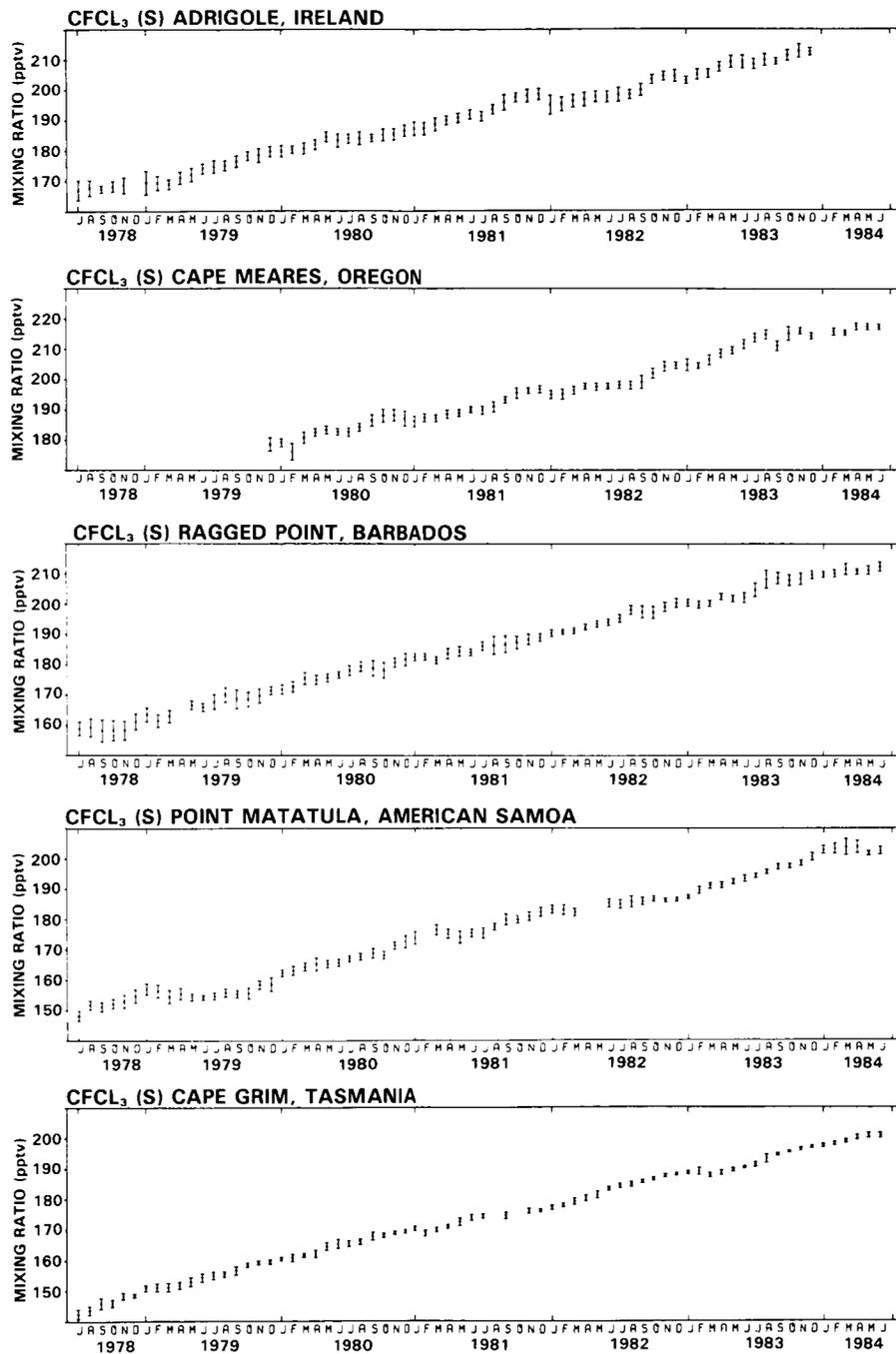


Figure 3-1. Monthly-mean mixing ratios and monthly variances of CFC-13 measured 4-times-daily on a gas chromatograph with a silicone column at the ALE/GAGE stations during the first 6 years of the ALE/GAGE network. The calibration factor used is 0.96 (see Prinn *et al.*, 1983a, 1983b; Rasmussen and Lovelock, 1983; Cunnold *et al.*, 1983a, 1983b; and Simmonds *et al.*, 1983 for further details). The CFC-13 trends based on the data from the first 5 years of the ALE/GAGE program (July, 1978-June, 1983) at Adrigole, Cape Meares, Ragged Point, Point Matatula, and Cape Grim are 4.4, 4.4, 5.0, 6.2 and 5.3% per year respectively. The Cape Meares trend is for 3.5 years of data while the other trends are for 5 years of data. The data for 7-83 to 6-84 are preliminary (R. Prinn, R. Rasmussen, F. Alyea, D. Cunnold, A. Crawford, P. Fraser, P. Simmonds and R. Rosen, private communication, 1985).

SOURCE GASES

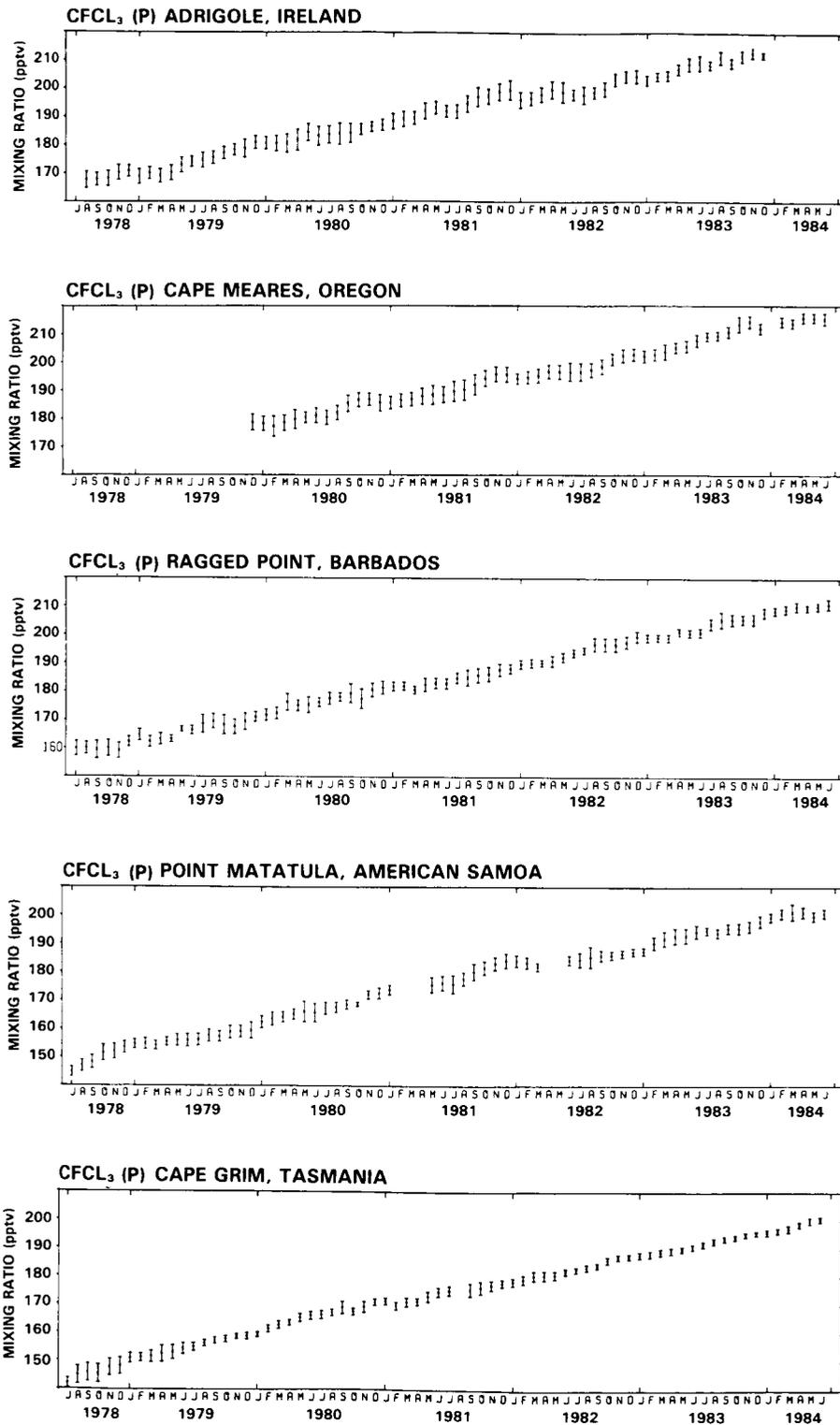


Figure 3-2. ALE/GAGE network data. As in Figure 1, but for CFC-11 measured on a Porasil column and with the 1978-1983 measured trends being 4.6, 4.3, 4.8, 5.7 and 5.2% per year at the 5 stations.

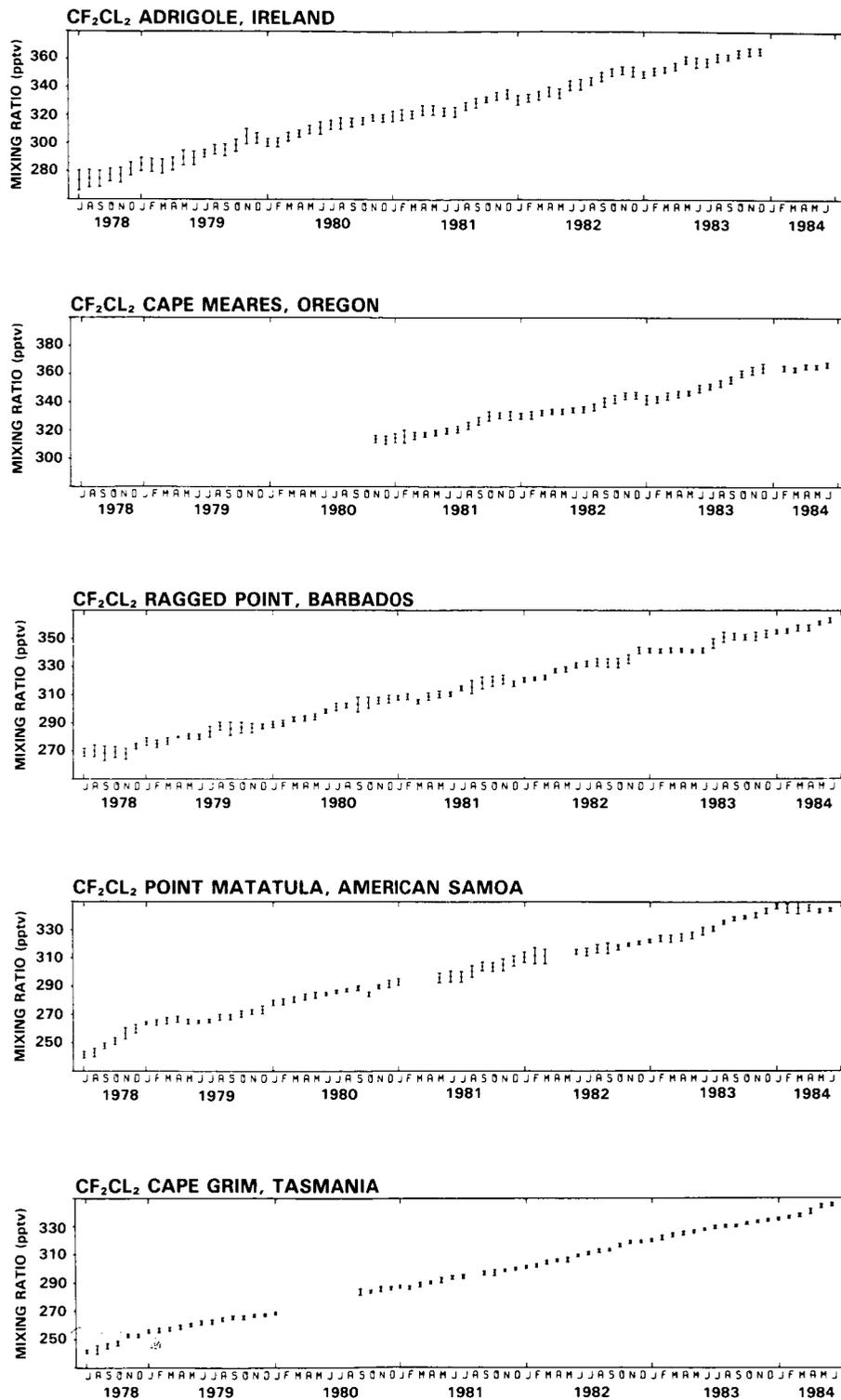


Figure 3-3. ALE/GAGE network data. As in Figure 1, but for CFC-12 measured on a Porasil column with a calibration factor of 0.95 and with the 1978-1983 measured trends being 4.7, 4.6, 5.2, 5.1 and 5.2% per year at the 5 stations.

SOURCE GASES

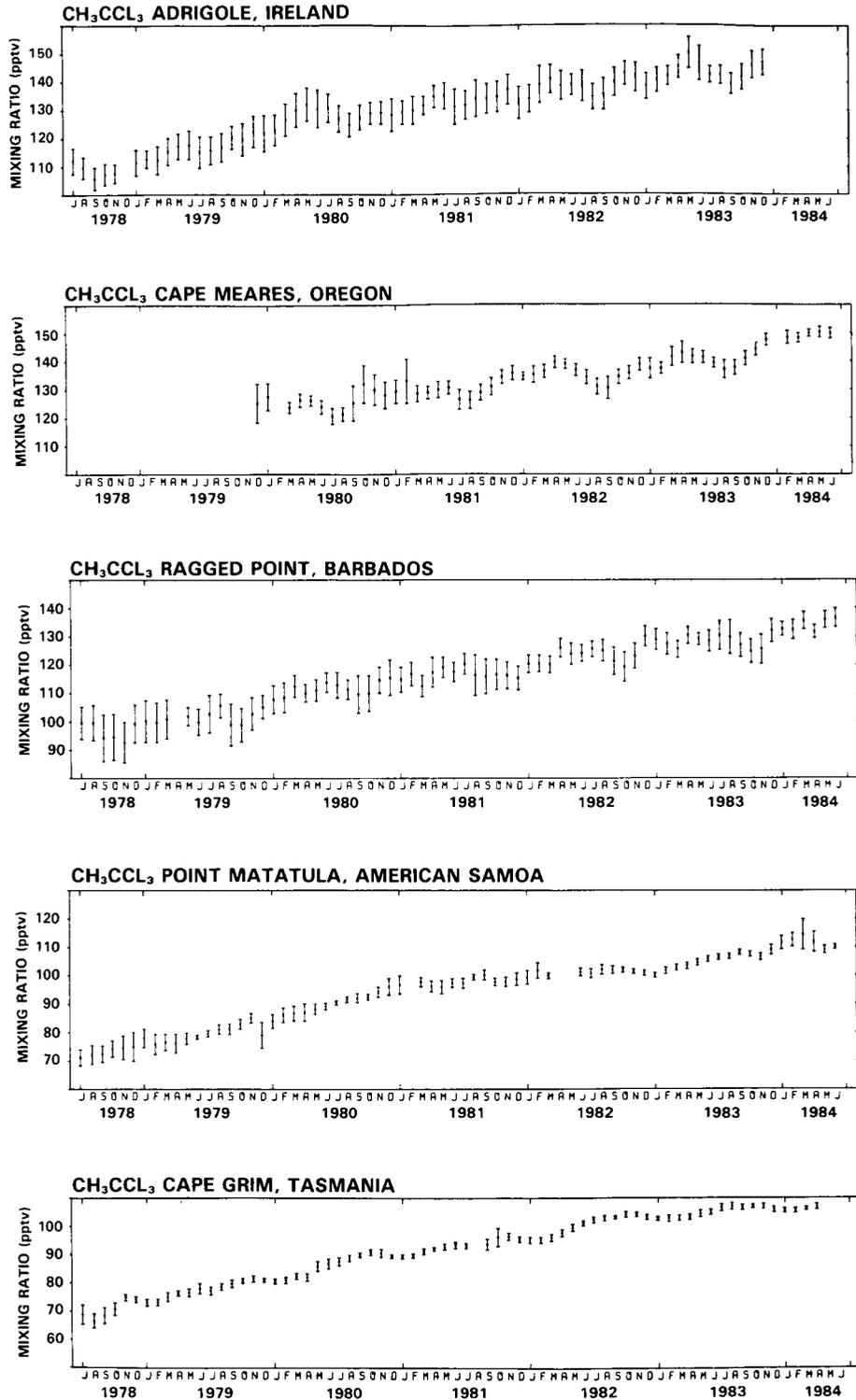


Figure 3-4. ALE/GAGE network data. As in Figure 1 but for CH₃CCl₃ measured on a silicone column with a calibration factor of 0.8 and with the 1978-1983 measured trends being 4.9, 3.8, 6.2, 8.1 and 8.1% per year at the 5 stations.

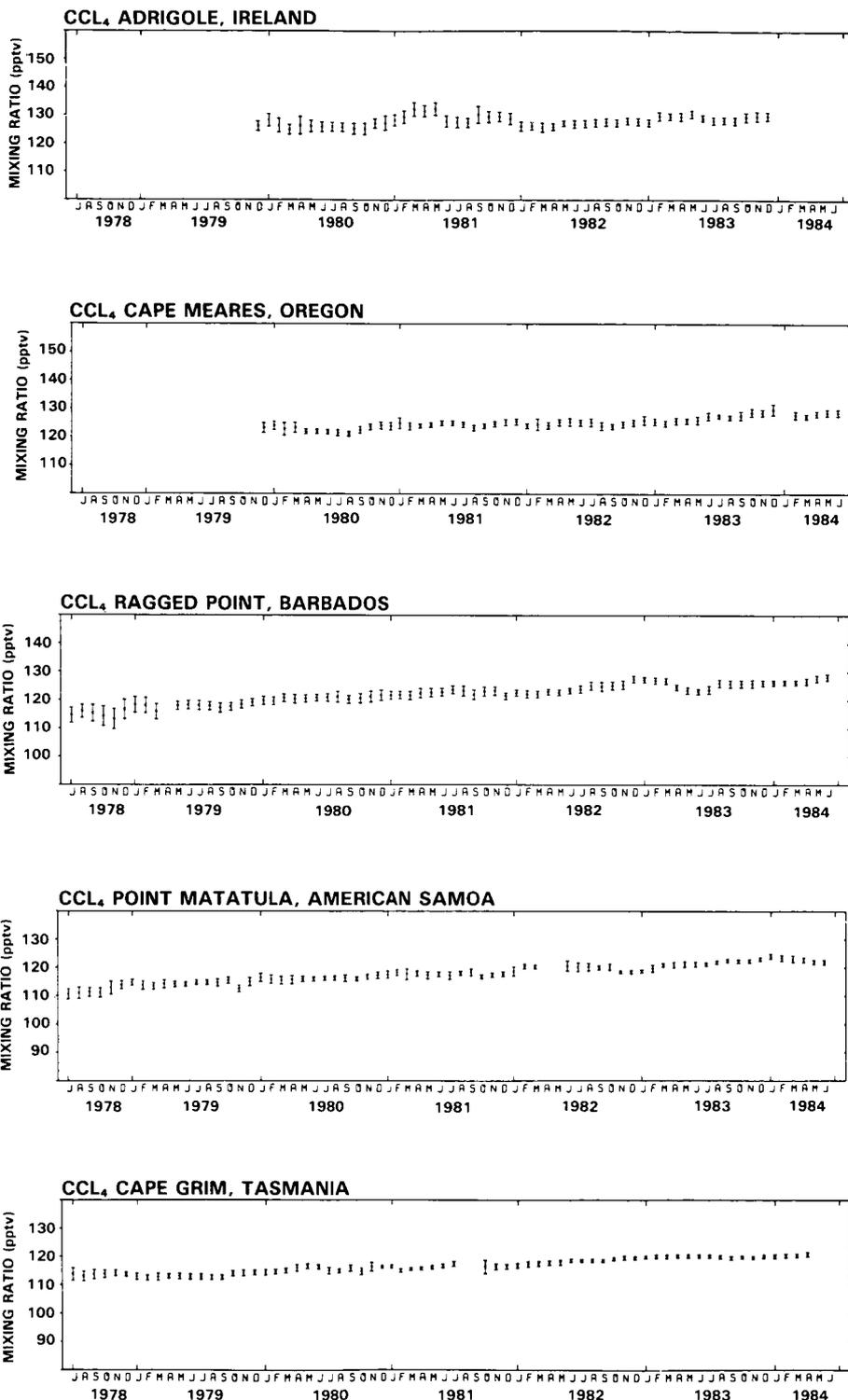


Figure 3-5. ALE/GAGE network data, as in Figure 1 but for CCl₄ measured on a silicone column with a calibration factor of 0.81 and with the 1978-1983 measured trends being 0.5, 0.8, 1.7, 1.4 and 1.3% per year at the 5 stations.

SOURCE GASES

CCl_4 : Use of carbon tetrachloride has been nearly stable for many decades, thus the atmospheric burden is relatively close to steady state and annual increases are relatively small. Release rates are not well-documented, but atmospheric observations appear to be consistent with a lifetime of ~ 50 yr., which could be explained by loss due to stratospheric photolysis with, perhaps, a contribution from hydrolysis in the oceans, (Simmonds *et al.*, 1983).

Distributions, trends and lifetimes for a wide range of halocarbons have been determined by various investigators, as summarized in Tables 3-1 and 3-2. Long-lived species presently at very low levels can potentially contribute significant concentrations of Cl and Br to the stratosphere, if release rates grow rapidly. As discussed below, CFC-113 ($\text{C}_2\text{Cl}_3\text{F}_3$) and CFC-22 (CHF_2Cl) are of particular interest, with their long lifetimes, increasing industrial applications, and rapidly rising atmospheric concentrations (Table 3-1B).

A number of bromine containing gases have been measured in the atmosphere remote from industrial or natural sources. Two brominated methane species, CH_3Br and CHBr_3 , are found to be the most abundant bromine-containing compounds (Table 3-2). The concentrations of CHBr_3 are quite variable because of its short atmospheric lifetime. Four other bromine containing trace gases are found at lower concentrations of around 1 to 4 pptv; these are CH_2Br_2 , CHBr_2Cl , CH_2BrCl and $\text{C}_2\text{H}_4\text{Br}_2$. Finally there are two industrial gases present in the atmosphere at about 1 pptv; these are CBrClF_2 (BCF) and CF_3Br both used as fire extinguishing compounds. Methyl bromide (CH_3Br) and the two fire extinguishing compounds are more abundant in the Northern Hemisphere compared to the Southern Hemisphere. These compounds have known industrial sources. The presence of relatively large amounts of the other bromine containing trace gases in the Southern Hemisphere suggests that the oceans may be a source for these compounds, except for $\text{C}_2\text{H}_4\text{Br}_2$. Bromine compounds have recently served as tracers of pollution associated with arctic haze (Rasmussen and Khalil, 1984c; Berg *et al.*, 1984; Khalil and Rasmussen, 1985c).

Since bromine is a very efficient catalyst for recombination of ozone, concentrations of organobromine species as low as ~ 100 ppt could be of interest to stratospheric chemists (Prather *et al.*, 1984). Current levels are below 25 ppt, but some species are increasing rapidly. The long-lived bromocarbons Halon 1301 (CF_3Br) and Halon 1211 (CBrClF_2), have enjoyed an expanding market in fire extinguishers for high technology, aircraft, and military applications. Hence, it might be expected that atmospheric concentrations may be increasing. Atmospheric concentration data for Halon 1301 are not available over a period of years. Concentrations of Halon 1211 in the atmosphere are rapidly rising, as documented by Khalil and Rasmussen (1985c) at the South Pole, the Arctic, and Cape Meares, Oregon (rate of increase 10–30% per year) and by Lal *et al.* (1985) in the upper stratosphere over France. Similarly, Lovelock (1985, private communication) observed ambient levels for Halon 1211 of only 0.16 pptv in 1978 at Cornwall, UK, but concentrations rose to 0.43 ppt in 1980 and 1.5 ppt in 1981.

There are no data establishing a trend for either CH_3Br or $\text{C}_2\text{H}_4\text{Br}_2$ in the atmosphere. Ethylene dibromide ($\text{C}_2\text{H}_4\text{Br}_2$) is an important industrial bromocarbon (see Table 3-2). Emissions arise from evaporation of leaded gasoline and from fumigation. Rates of use in both applications are declining, however, and the lifetime is relatively short (~ 1 yr.), hence concentrations of this species are unlikely to increase significantly in the near future. Methyl bromide (CH_3Br), the second most abundant organobromine gas, has also a relatively short lifetime (~ 3 yr.) (Logan *et al.*, 1978; Yung *et al.*, 1980). Sources from leaded motor fuel are currently in decline (Bauer, 1979). It seems unlikely that use of CH_3Br in fumigation can grow rapidly, due to the high toxicity of the gas, and about half of methyl bromide emissions appear to be of natural origin (Yung *et al.*, 1975; Yung *et al.*, 1980). Hence there is not expected to be significant future increase in the concentration of CH_3Br .

SOURCE GASES

Table 3-1A. Measured Distributions of Selected Halocarbons

COMPOUND	DATE	CONC \pm SD pptv	LAT	NH AVE \pm SD pptv	SH AVE \pm SD pptv	GLBL AVE \pm SD pptv	REF
CCl ₄	12/81			135	128		1
	2/81	150 \pm 3	20				2
	6/81	100	53				11
	1/80			121	115	118	26
	5/82	150 \pm 2	70	151			12
	11/81	146 \pm 1	30°S-42°S		145		13
CHCl ₃				30	19	25	9
				45	16	26	24
	12/81			21	11		1
	2/81	32 \pm 4	20	26			2
	11/81	21 \pm 3	30°S-42°S		18 \pm 2		13
	1978			29 \pm 7.0	29 \pm 4	29	15
CH ₂ Cl ₂	12/81			38	21		1
CH ₃ Cl	12/81	630	40°N-32°S				5
	1981	589 \pm 43	71				3
	11/81	617 \pm 9	30°S-42°S				13
CH ₃ CCl ₃	12/81			156	116		1
	2/81	149 \pm 3	20				2
	1981	170 \pm 9	70				3
	11/81	123 \pm 0.6	30°S-42°S				13
	1978			117 \pm 4.0	90 \pm 3		15
	1/80			114	83	98	25
C ₂ HCl ₃	12/81			12	< 3		1
	1981		71	18			3
	1981	16 \pm 15	70				3
				11			12,22
C ₂ Cl ₄	12/81			29	5		1
	2/81	60 \pm 7	20				2
	1981		71				3
	1981	87 \pm 28	70	89			3
	11/81	9 \pm 1	30°S-42°S		9 \pm 1		13
	1978			56 \pm 11	14 \pm 3	35	15
			90			22	
CH ₂ ClCH ₂ CCl	12/81			37	14		1
CF ₄ (CFC-14)	1979					70 \pm 7	16
	1979	64 \pm 2	90°S				23
	1984	72 \pm 2	90°S				23
C ₂ F ₆ (CFC-116)	1979			4	3.5	4 \pm 0.9	16

SOURCE GASES

Table 3-1A. Measured Distributions of Selected Halocarbons. — Continued

COMPOUND	DATE	CONC ± SD pptv	LAT	NH AVE ± SD pptv	SH AVE ± SD pptv	GLBL AVE ± SD pptv	REF
SF ₆	12/81			0.9	0.8		1
CClF ₃ (CFC-13)	1979			3.2	3.6	3.4 ± 0.6	16
CCl ₂ F ₂ (CFC-12)	12/81			305	282		1
	2/81	326 ± 2	20				2
	1981	339 ± 6	70				3
	5/82	353 ± 3	70				12
	11/81	321 ± 1	30°S-42°S				13
	1978			274 ± 2	255 ± 4		15
	1/80			296	274	285	7
CCl ₃ F (CFC-11)	12/81			186	172		1
	1/80					168	8
	1981	199 ± 3	70				3
	5/82	205 ± 2	70				12
	6/81	191	53				11
	11/81	186 ± 1	30°S-42°S				13
	1978			161 ± 1	148 ± 2		15
	1/80			174	160.5	168	6
CHClF ₂ (CFC-22)	2/81	64 ± 1	20				2
	1981	71 ± 4	70				3
	11/81	58 ± 0.6	30°S-42°S				13
	1978			42 ± 1	36 ± 1	39	15
				73			12
C ₂ ClF ₅ (CFC-115)	1979	4.1					16
C ₂ Cl ₂ F ₄ (CFC-114)	12/81			14	13		1
C ₂ Cl ₃ F ₃ (CFC-113)	12/81			23	21		1
	2/81	21 ± 0.5	20	19 ± 0.4			2
	11/81	17 ± 1	30°S-42°S		17 ± 11		13
	1978			13 ± 0.8	12 ± 0.6		15
				17	11	14	19
				16	12	14	20,24
	5/82	23 ± 4	70				12

SOURCE GASES

Table 3-1B. Reported Trends for Selected Halocarbon Concentrations

COMPOUND	DATE	INC %/yr \pm SD	INC ppt/yr \pm SD	LIFETIME \pm SD (YEARS)	REF
CCl ₂ F ₂ (CFC-12)	12/81		26.0 \pm 5	100 +100/-40	1
	1/80	6.0	17.1	greater than 81	7
			9.0 \pm 2		19
	1980			135	17
	1980			120	14
CCl ₃ F (CFC-11)	12/81		15.0 \pm 3	60 + 40/-20	1
	1/80	5.7	9.6	78	6
	1/80			75	8
			10.0 + 1/-3		19
	75-81	6-7		60	14
				11	
CF ₄ (CFC-14)	79-84	~2	1.3 \pm 0.6	? ~ 10 ⁴	27
CHClF ₂ (CFC-22)		11.7			4
			10 - 11	75 + 15/-10	11
					11
C ₂ Cl ₃ F ₃ (CFC-113)		10.0			20,24
CCl ₄	12/81		6.0		1
	1/80	1.8	2.1	52	26
CHCl ₃				0.50	9
	11/81			0.33	13
CH ₂ Cl ₂	12/81			0.9 \pm 0.3	1
CH ₃ CCl ₃	12/81		13.0 \pm 3	9 + 2/-1	1
			13.2 + .8/-1.2		19
	11/81				13
	1/80	8.7	8.6	6.5 to 9	25
C ₂ Cl ₄	12/81			0.6 \pm 0.2	1
CH ₂ ClCH ₂ CCl	12/81			0.6 \pm 0.2	1

1. Singh, *et al.*, 1983a.

2. Rasmussen and Khalil, 1981a.

3. Rasmussen and Khalil, 1983a.

4. Khalil and Rasmussen, 1981.

5. Singh, *et al.*, 1983b.6. Cunnold *et al.*, 1983a.7. Cunnold *et al.*, 1983b.8. Fraser *et al.*, 1983.9. Khalil *et al.*, 1983.10. Brice *et al.*, 1982.

11. Rasmussen and Khalil, 1983d.

12. Rasmussen *et al.*, 1982a.13. Owens *et al.*, 1982.

14. Rasmussen and Khalil, 1982.

15. Penkett *et al.*, 1981.

16. Khalil and Rasmussen, 1983.

17. Rasmussen *et al.*, 1981c.

18. Rasmussen and Khalil, 1983c.

19. Rasmussen *et al.*, 1983b.

20. Rasmussen and Khalil, 1984a.

21. Khalil and Rasmussen, 1985d.

22. Khalil and Rasmussen, 1985e.

23. Prinn *et al.*, 1983a.24. Prinn *et al.*, 1983b.25. Simmonds *et al.*, 1983.

26. Cicerone, 1979.

SOURCE GASES

Table 3-2. Atmospheric Concentrations of Bromo- and Iodo Carbons

COMPOUND	DATE	CONC \pm SD pptv	LAT	NH AVE \pm SD pptv	SH AVE \pm SD pptv	GLBL AVE \pm SD pptv	REF
CH ₃ I	1981	1.3 \pm 0.2	60°N			0.8	4
	1981	2.5 \pm 0.8	22°N				4
	1981	3.4 \pm 0.5	8°N				4
	1981	2.6 \pm 0.9	14°S				4
	1981	2.4 \pm 1.3	42°S				4
	1981	1.8 \pm 0.4	90°S				4
	1981	7.0 \pm 0.5	15°N				4
	1981	22.0 \pm 5.0	60°N				4
	1981	12.0 \pm 3.0	34°S				4
		1981			3.1 \pm 0.3		2.2 \pm 0.5
CH ₃ Br	1981	10.9 \pm 0.9	72°N				2
	1983	9 - 14	72°N				7
	3/83	11 \pm 4	60-80°N				6
	11/84	7.5	90°S				1
CHBr ₃	3/83	2 - 46	60-80°N				6
	11/84	7.5	90°S				1
CH ₂ Br ₂	1981	5.0 \pm .3	72°N				2
	1983	4.7 - 5.6	72°N				7
	3/83	3 - 60	60-80°N				6
CH ₂ BrCl	1981	2.5 \pm .3	72°N				2
	1983	2.3 - 2.8	72°N				7
	11/84	2.5	90°S				1
CHBr ₂ Cl	11/84	0.70	90°S				1
C ₂ H ₄ Br ₂	1981	1.24 \pm .30	72°N				2
	1983	1.0 - 1.9	72°N				7
	3/83	1 - 37	60-80°N				6
CF ₃ Br	11/84	1.0	90°S				1
CBrClF ₂	11/84	1.10	90°S				1
	1981	1.09 \pm 0.10	72°N				2
	2/1985	2.00	44°N				3
	9/1982	1.03	72°N				3
	9/1983	1.31	72°N				3
	10/84	1.49	72°N				3
	1983	0.9 - 1.2	72°N				7
Br - total organic	1981	30	72°N				2
	11/82	7.6 \pm 3.0	72°N				5

1. Khalil and Rasmussen, 1985c.
2. Rasmussen and Khalil, 1984c.
3. Lal *et al.*, 1985.
4. Rasmussen *et al.*, 1982b.

5. Berg and Sperry, 1983.
6. Berg *et al.*, 1984.
7. Rasmussen and Khalil, 1984c.

3.1.2 Sources

Industrial Production and Use

Table 3-3 presents a summary list of industrial halogenated species which have been observed in the free atmosphere, along with estimated source strengths. No organization currently has access to truly global industrial production data for halocarbons. The chlorofluoromethanes CFC 11 and 12 (CFCl_3 , CF_2Cl_2) are the only compounds for which data covering a large fraction of the market are published, and for which emission estimates are routinely made. There is only very sparse information for the other halocarbons. Available data and estimates on production, current and historic, for the chemicals listed in Table 3-3 are described below and factors likely to influence future use are discussed. Of the industrially produced halocarbons considered here, only the methyl halides (CH_3Cl , CH_3Br , CH_3I , CH_2Br_2 , etc.) appear to have significant natural sources (Singh *et al.*, 1983a).

CFC 11 (CFCl_3) and CFC 12 (CF_2Cl_2)

The Fluorocarbon Program Panel (FPP) of the Chemical Manufacturers Association (CMA) sponsors publication of an annual report of production for CFC 11 and CFC 12 by 20 companies representing production in North America, South America, Western Europe, Japan, Australia, Africa, and India. The data for 1960-1984 are summarized in Figure 3-6. The production of CFCs 11 and 12 by these companies fell by 7% in 1982 relative to 1981, to 599 kt, but rose by 8% in 1983 to 644 kt and rose by an additional 8% in 1984 to 694 kt (CMA, 1985). Thus in the last two years production rose by 16%, while remaining slightly below (~13%) the 810 kt produced by reporting companies in 1974, the peak year.

The FPP formerly attempted to estimate production in the rest of the world by extrapolation of data published for the USSR for the period 1968-75, which suggested 18% annual growth during that period. Continued use of this extrapolation could not be justified in the absence of more recent data for the USSR. Data for the People's Republic of China and the countries of Eastern Europe are lacking entirely. Consequently, no world production estimate was made for 1983 and the FPP does not plan to resume estimating world production until credible CFC production data for these countries become available. It is still considered that production by the companies reporting to CMA represents 80-85% of the world total, but this fraction is not well known and may be expected to change with time. Earlier FPP estimates of total world production of CFC-11 and CFC-12 showed 1982 values to be only 7% below the 1974 peak, and therefore by extension, the 7% growth in 1983 would result in values comparable to 1974. Since these estimates (CMA, 1983) probably overestimated growth in Soviet manufacture of CFC-12, world production of CFC's probably did not achieve levels of the peak year (1974) prior to 1984. The uncertainties in the world estimates are substantial, and we must fall back on careful monitoring of the atmosphere to provide the best information on worldwide emissions.

FPP production figures are broken down by use-category and CFC emissions to the atmosphere are then calculated. For each use an estimate has to be made for product lifetime, for rate of loss of CFC during use, and for fate upon disposal. The emission calculations are revised as new information becomes available (Gamlen *et al.*, 1985). For example, the rate of diffusion of CFC 11 from closed-cell foams has been reported recently to be slower than previously estimated (Khalil and Rasmussen, private communication, 1985). The CMA data show that the pattern of usage of CFC 11 and CFC 12 has changed substantially since 1976 with a decline in aerosol usage and an increase in other applications. Delay times between production and eventual release to the atmosphere have therefore grown somewhat.

SOURCE GASES

Table 3-3. Atmospheric Halocarbons (partial list)

Substance	Measured concentration (pptv)	Time (year)	Est. global industrial production × 10 ⁶ kg	Year	Reference	Est. atmospheric lifetime years (NAS 1984)
CFC 11 (CCl ₃ F)	200	1983	310	1982	1,8	65
CFC 12 (CCl ₂ F ₂)	320	1983	444	1982	1,8	120
CFC 13 (CF ₃ Cl)	~ 3.4	1980	—	—	10	400
CFC 22 (CHCl ₂ F)	~ 52	1980	206	1984	2,7	20
CFC 113	~ 32	1/85	138-141	1984	2,5	90
CFC 114	—	—	13-14	1984	2	180
CFC 115	4	1980	—	—	10	380
CH ₃ CCl ₃	~ 120	1983	545	1983	3,11	6.5
CFC 116	~ 4	1980	—	—	10	> 500
CCl ₄	~ 140	1979	~ 830	1983	3,12	50
CH ₃ Cl	630	1980	~ 500	1984	3,6	~ 1.5
CH ₃ I	~ 1	1981	—	—	9	0.02
CBrClF ₂	~ 1.2	1984	(~ 5?) [‡]	—	4	25
CBrF ₃	~ 1	1984	7-8	1984	2,4	110
CH ₃ Br	9.0	1984	—	—	4	2.3
CH ₂ BrCl	3.2	1984	—	—	4	—
CHBr ₂ Cl	0.9	1984	—	—	4	—
C ₂ H ₄ Br ₂	~ 1	1984	—	—	4	~ 1
CHBr ₃	~ 2	1984	—	—	4	—

[‡] Estimated release from observed atmospheric increase, uncertain delay between industrial production and release to the atmosphere.

1. CMA, 1984.
2. DuPont, private communication, 1985.
3. ICI, private communication, 1985.
4. Khalil and Rasmussen, 1985a [mean of arctic and antarctic values, fall, 1984].
5. Khalil and Rasmussen, 1985d.
6. Rasmussen *et al.*, 1980.
7. Khalil and Rasmussen, 1981.
8. Cunnold *et al.*, 1983 a, b; Cunnold, 1984.
9. Rasmussen *et al.*, 1982.
10. Penkett *et al.*, 1981.
11. Prinn *et al.*, 1983b; Khalil and Rasmussen, 1984a.
12. Simmonds *et al.*, 1983; Rasmussen and Khalil, 1981.

Other Halocarbons

Concern over depletion of stratospheric ozone by chlorine is not restricted to CFC-11 and 12 alone. Numerous other halocarbons discussed below contribute to the accumulation of chlorine in the stratosphere. Attention focuses generally on the long-lived CFCs (11, 12, 22, 113, 114) and on CH₃CCl₃, which are likely to become important sources of stratospheric chlorine in the next century. CFC-113 represents as much as 15% of the current production of long-lived halocarbons, due to rapid growth occurring since

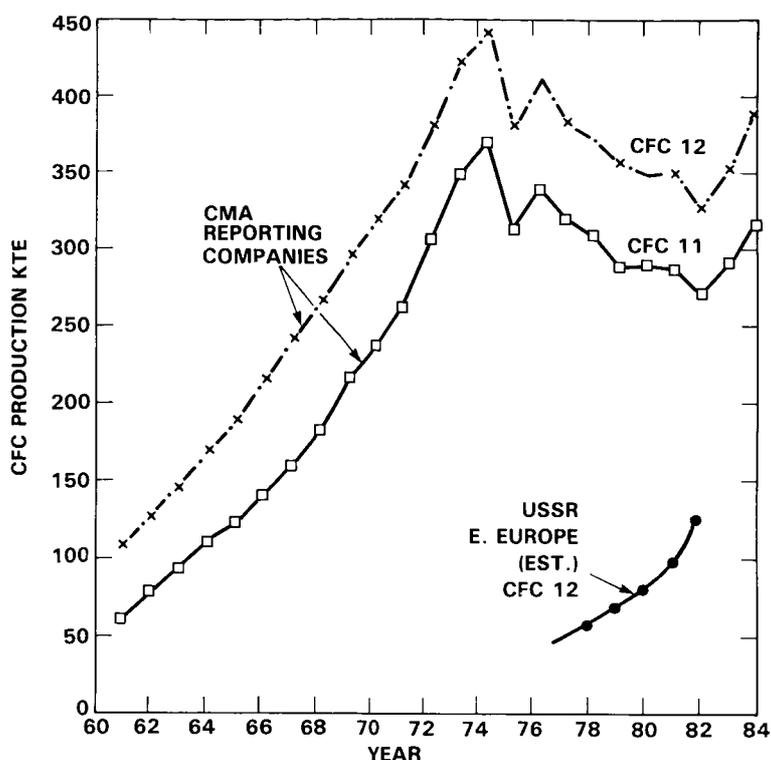


Figure 3-6. Chlorofluorocarbon production history for CFC-11 and CFC-12, 1961-84 for CMA reporting companies. Soviet Union/Eastern European production for CFC-12 is estimated separately. USSR production is based on Borisenkov and Kazadov, 1977 with estimates continued by CMA to include Eastern Europe from 1976 through 1982 (CMA, 1984).

1974. If CFC-113 is counted along with CFC-11 and CFC-12, it appears that there has been an overall increase in world-wide production of long-lived CFCs above that of the former peak year, 1974. We now discuss industrial sources of these species.

CFC 22 (CHClF_2)

Refrigeration is the major use of CFC 22 but a significant portion, about 35% of total production, is used as a chemical intermediate to prepare tetrafluoroethylene, which in turn is polymerized to fluoropolymers. Limited CFC 22 production data have been reported for several years. Growth in fluoropolymer production (with little emission of CFC 22 to the atmosphere) accounts for much of the recent growth in CFC 22 production. It has been estimated that 102 , 163 , and 206×10^6 kg of CFC 22 were produced globally in 1977, 1981, and 1984 respectively (NASA 1979, DuPont, 1983).

CFC 113 ($\text{CCl}_2\text{FCClF}_2$)

CFC 113 is used largely as a solvent to clean and deflux sophisticated electronic assemblies and components. Lower-cost cleaning systems, such as chlorocarbons and aqueous systems, also compete for this application. Historical production data are not available for CFC 113. DuPont (1981) estimated that about 70 , 79 , and 91×10^6 kg were produced globally in 1977, 1978, and 1979. Production of CFC 113 has increased rapidly in recent years, but its growth may level off as the market matures, and global production in 1984 has been estimated to be about 140×10^6 kg (DuPont, private communication, 1985). Its future use is vulnerable to competing systems, changes in electronics technology, and possible requirements to reclaim the solvent.

SOURCE GASES

Table 3-4. Global Production of CH₃CCl₃ (excluding USSR and Eastern Europe)

Year	Production/Sales CH ₃ CCl ₃ (10 ⁶ kg)	
	ICI (1985) (Production)	Prinn <i>et al.</i> , (1983b) (Sales)
1976	475	—
1977	490	483.6
1978	520	497.5
1979	580	535.5
1980	580	544.2
1981	570	544.2
1982	540	—
1983	545	—

CFC 114 (CClF₂ CClF₂)

CFC 114 has limited use as an aerosol propellant of perfumes and colognes, as a refrigerant, and as an intermediate to prepare chloropentafluoroethane (CFC 115). Its production has remained relatively constant over the past 6 years at about 13×10^6 kg (ICI, private communication, 1985).

Methyl Chloroform (CH₃CCl₃)

Stabilized 1,1,1-trichloroethane (methyl chloroform) has been marketed since the early 1960's. Its principal use has always been the industrial degreasing of metallic or metaloplastic pieces. It is widely used for cold cleaning processes in the engineering industry. It is also used as a solvent in adhesives, varnishes and paints where low flammability and low toxicity are important. Sales of methyl chloroform grew rapidly in the 1960's and early 1970's when it replaced tri- and perchloroethylene and CCl₄ in many industrial applications. This replacement process is virtually complete in Western countries. Estimated global sales have leveled off since 1979, due at least in part to increasing efficiency of usage and to solvent reclamation (see Table 3-4).

Carbon Tetrachloride (CCl₄)

It is difficult to define the global capacity for production of carbon tetrachloride because it is co-produced with other chemicals. One industry estimate puts current capacity at 1150×10^6 kg per annum. Carbon tetrachloride is used predominantly as a chemical intermediate in the production of CFCs 11 and 12, leading to relatively little emission of CCl₄ to the atmosphere. Using the reported CMA figures for 1983 production of CFCs, the quantity of CCl₄ used in this application is inferred to be 778×10^6 kg. Various estimates put other uses and fugitive emissions of CCl₄ at 5–10% of total sales. This would indicate that the 1983 total production (excluding USSR, Eastern Europe and People's Republic of China) was 830×10^6 kg, of which only $40\text{--}80 \times 10^6$ kg would be likely to be emitted to the atmosphere (cf. Simmonds *et al.*, 1983). Sales of CCl₄ for direct use have declined significantly in the West because of concerns about its

toxicity. A small fraction is still used as a solvent in chemical and pharmaceutical production processes. Use as a grain fumigant is declining. However, there is some indication that release rates may still be substantial in Eastern Europe, the USSR or China. Annual release of at least 90×10^6 kg is needed to explain atmospheric data for CCl_4 from ALE (Simmonds *et al.*, 1983).

Brominated Compounds

Atmospheric bromine (Table 3-3) is dominated by methyl bromide (CH_3Br) and bromoform (CHBr_3). The bromoform is believed to be mainly of natural origin, and CH_3Br about 50% natural. As discussed above, anthropogenic emissions of ethylene dibromide (EDB) and CH_3Br are probably declining. They have been used as grain fumigants, and both are emitted by automobiles using leaded gasoline.

As discovered earlier, two long-lived industrial brominated compounds (Halons 1211 and 1301) are currently of greater interest due to their rapidly increasing usage.

Halon 1211 (CBrClF_2)

The relatively high boiling point and low vapor pressure of Halon 1211 make it ideal for use in portable fire extinguishers. Flame extinction can be very rapid due to the high activity of Br atoms as combustion inhibitors. The growth of the Halon 1211 market has been as a replacement agent for CCl_4 and CO_2 extinguishers. Halon 1211 has been commercially available for more than 20 years but world sales did not reach significant volumes until the early 1970's. One industrial estimate (ICI, private communication, 1985) notes that the initially high growth rates of the 1970's have not been maintained. However, no data on current production for Halon 1211 are available from industry sources. The atmospheric data discussed in Section 3.1.1 imply release of about 5 kt per annum and rapid growth.

Halon 1301 (CBrF_3)

Halon 1301 is used almost exclusively as a fire extinguisher in total-flooding applications where water and carbon dioxide are unacceptable, such as in computer rooms, marine engines, art museums, etc. A small amount of the chemical is used as a refrigerant in special applications. DuPont (1978) estimated 1976 U.S. production to be about 1.4 kt which suggests 1976 global production was 1.4–3.0 kt. World production in 1984 was estimated to be 7–8 kt (DuPont, private communication, 1985). A large portion of increased use over recent years was for the fire protection of large oil and gas pipeline projects, and an industry estimate (DuPont, private communication, 1985) expects slower growth in fire protection applications of Halon 1301 in the future.

Methyl Chloride (CH_3Cl)

It is generally accepted that the industrial production of methyl chloride is far outweighed by releases from the oceans and from burning vegetation. Recent estimates of the total source are 2–5 MT per year (see for example, Logan *et al.*, 1981; Crutzen *et al.*, 1983), based on calculation of global reaction rates with OH. One estimate puts annual industrial production worldwide at 0.5 MT, or less than ~25% of global sources (ICI, private communication, 1984). Quantitation of the major sources is highly uncertain at present, and human activity (biomass burning) is likely to be a major contributor.

3.1.3 Discussion

Atmospheric Inventory

For a certain category of trace gases, observations of the changing atmospheric burden may be used to derive a globally integrated source for the gas. A requirement for such analysis is that the uncertainty in calculated atmospheric losses of the gas be much less than new releases to the atmosphere. These condi-

SOURCE GASES

tions are applicable to most halocarbons whose atmospheric concentrations are far from steady-state levels, due either to long atmospheric lifetimes (~ 100 yrs.) and/or to rapid growth in release rates.

The CFCs 11 (CFCl_3) and 12 (CF_2Cl_2) have received the most attention. Their long lifetimes allow atmospheric observations to record cumulative release with moderate accuracy. Rowland (1982) pointed out disparities between estimated release for CFC-12 and the observed increase in atmospheric concentrations, based on surface measurements at two stations (Oregon and South Pole) for limited times over several years. This analysis has been confirmed by continued observations by more researchers using expanded observing networks. The observed atmospheric trend in CFC-11 is relatively consistent with CMA estimates of release (Cunnold *et al.*, 1983a; Fraser *et al.*, 1983a), whereas CFC 12 appears to require a substantial source from the USSR and Eastern Europe (Cunnold *et al.*, 1983b). The increase in the Eastern European source must, however, be less than the 18% compounded annual growth assumed since 1975 in pre-1983 CMA projections.

Inventories of methyl chloroform (CH_3CCl_3) and carbon tetrachloride (CCl_4) have also been analyzed using the ALE data (Prinn *et al.*, 1983b; Simmonds *et al.*, 1983). The global distribution and trend are consistent with previous flask measurements of CH_3CCl_3 (Rasmussen and Khalil, 1981a,c,d). Global emissions may be determined for these gases with somewhat less accuracy than for the CFCs, since they are closer to a steady-state between emission and atmospheric loss. As noted earlier, the atmospheric lifetime for CH_3CCl_3 is relatively short, 6.5–10 years (Khalil and Rasmussen, 1984a; ALE data updated) and thus photochemical losses (uncertain to at least $\pm 25\%$) play a more dominant role in the global annual inventory than for CFC's. ALE analysis notes that industry estimates of CH_3CCl_3 releases are consistent with observations over the 5 years of the ALE record if some delay in release of early production is considered in the early years. The derived range of lifetimes for CH_3CCl_3 , 6.5–10 years, implies emissions of 500–600 kt per year.

Data for CH_3CCl_3 from the ALE program have helped to define the global loss rates for other gases removed from the atmosphere by reaction with the OH radical, e.g. CH_4 . The idea behind this analysis was proposed by Lovelock (1977) and followed up by a variety of authors (Crutzen and Fishman, 1977; Derwent and Eggleton, 1981; Makide *et al.*, 1981; Logan *et al.*, 1981). A lifetime of 5.5 yr. is calculated by the model of Logan *et al.* (1981), using updated chemical reaction rates, reasonably consistent with the ALE result of 6.5 yr. from the inventory method. Models using updated chemical rates may be expected therefore to provide fairly good estimates for the global OH distribution and hence for the removal rates of important trace gases such as CH_4 (see below).

Global burdens of CCl_4 are also close to steady state, despite a longer atmospheric lifetime (~ 50 yrs.), because the gas has a much longer history of sustained atmospheric release (Simmonds *et al.*, 1983). In this case industry estimates of release in the reporting (i.e., Western) countries can account for only half of the 90 kt per year needed to maintain the observed atmospheric increase.

As discussed above, CFC-113 ($\text{C}_2\text{Cl}_3\text{F}_3$) is increasing rapidly in the earth's atmosphere. Recent measurements at Barrow, Alaska since mid-1983 yield a growth rate of $14 \pm 1\% \text{ yr}^{-1}$, while an earlier time-series at the South Pole (1/79–1/82) gave $\sim 10\% \text{ yr}^{-1}$ (Khalil and Rasmussen, 1985b). Industrial production data (see above) suggest rapid growth in the manufacture of CFC-113, $\sim 13\% \text{ yr}^{-1}$ during 1977–1979 and $\sim 10\% \text{ yr}^{-1}$ 1979–1984. The global burden is far from a steady state distribution and large increases in the atmospheric burden appear inevitable. Hence, even though present concentrations are less than 10% of CFC-11 and CFC-12, industrial emissions and atmospheric burdens of CFC-113 would appear to merit careful scientific scrutiny in the next 10 yrs.

The observed atmospheric growth rate of CHClF_2 reported for the late 1970's (11–12% yr^{-1} , Khalil and Rasmussen, 1981) is quite consistent with the industrial production data cited above for this same period. Whether slower growth of industrial production in the present decade ($\sim 8\% \text{ yr}^{-1}$ for 1981–1984, see above) is reflected in a turn-down in the rate of atmospheric increase has not yet been reported. If the change in end-use, away from refrigeration toward Teflon polymer production, has actually resulted in reduced fugitive emissions, a corresponding reduction in the atmospheric growth rate should now be discernible. However, use in the USSR and Eastern Europe is unknown and could be significant. CFC-22 is a major atmospheric halocarbon (Table 3-1) and it also merits careful scrutiny.

Six years of data at the South Pole (Khalil and Rasmussen, 1985c) indicated that atmospheric CBrClF_2 (Halon 1211) is increasing very rapidly at $\sim 22 (\pm 5)\% \text{ yr}^{-1}$. The atmospheric level in late 1984 was 1.1 pptv at the South Pole, and 30% higher in the Arctic, consistent with production and use in high technology, fire-extinguishing applications in the industrialized Northern Hemisphere. Continued growth at the present rate for another decade would bring CBrClF_2 levels to > 10 pptv, surpassing identified natural sources of stratospheric bromine. Trend data for other atmospheric bromine gases have not yet been reported but rapid increases for CF_3Br might be anticipated based on estimates of production. Khalil and Rasmussen (1985) estimate total gaseous (organic) bromine at a current level 22 pptv in late 1984, of which perhaps 20–50% is of anthropogenic origin.

The recent advent of widespread use for CBrClF_2 and CF_3Br ensure substantial growth in future atmospheric burdens, since lifetimes are long, 25 yr. for CBrClF_2 and 100 yr. for CF_3Br (Molina *et al.*, 1982; Prather *et al.*, 1984), and present burdens are therefore much smaller than steady-state values. The atmospheric levels and industrial production of Halon fire suppressants therefore should be monitored closely, even though accumulation of damaging levels (50–100 ppt) would take a long time (Prather *et al.*, 1984).

Regional Relative Source Strengths

Emissions of halocarbons from major source regions may be derived from the relative enhancement of trace gas concentrations in air masses influenced by these source areas. The sampled air mass may be viewed as an integrator of emissions on a regional scale. Such studies allow direct verification of source estimates. For example, a recent study attempted to derive the urban, combustion-related source of methane from the elevated concentrations of CH_4 and CFC 11 in city centers around the world (Blake, *et al.* 1984).

Analysis of the reported ALE data by Prather (1985) has shown that, with a sufficient number of observations during pollution episodes, accurate relative source strengths may be derived for European emissions of CFC-11, CFC-12, CCl_4 and CH_3CCl_3 using data from Adrigole, Ireland. The temporal correlation of variations in the five ALE trace gases provides information on both the spatial association of sources and on the duration and recurrency of pollution events. Atmospheric measurements must be made at high frequency in order to obtain meaningful results using this analysis.

At Adrigole all the halocarbons exhibit similar patterns: the full width at half-height, of a pollution event averages 2 days although enhanced concentrations may persist for nearly a week. These events recur at roughly 5 to 8 day intervals. Variations of concentrations of the major halocarbons (CFC-11, CFC-12, and CH_3CCl_3) are highly coherent. Evidently, major pollution events accumulate quantitatively comparable emissions of these gases. Carbon tetrachloride, on the other hand, is not fully coherent with the other halocarbons. One interpretation would place major CCl_4 sources in spatially distant regions (e.g., Eastern Europe) as compared with those of major CFC sources (e.g., Western Europe).

SOURCE GASES

European source strengths for CFC-12, CH_3CCl_3 , and CCl_4 , relative to that for CFC-11, are reported in Table 3-5, which also includes results of similar analyses for ALE data from Cape Meares, Oregon and Cape Grim, Tasmania (Prather, 1985). These latter two stations record pollution events less often and of smaller magnitude than observed at Adrigole, making the analyses there more uncertain. The data show that release patterns for the CFCs are similar for Europe, Western U.S. and Australia although Australian releases of CFC-12 are noticeably smaller with respect to CFC-11. More importantly, the global inventory for CFCs indicate a substantially larger source of CFC-12, relative to CFC-11, than is found by time series analysis of ALE data for any station. Since the effluents from the Soviet Union and developing countries are not sampled by ALE stations it appears that these countries play a relatively important role in world use of CFC-12, confirming suggestions made in earlier studies (Rowland, 1982; Cunnold *et al.*, 1983b) of the global inventory.

Emissions of CH_3CCl_3 , measured relative to CFC-11, are clearly variable among the continents: Europe is about equal to the global mean value, the Western U.S. is a factor of 1.3 above global mean, and Australia a factor of 2 below. Carbon tetrachloride shows a relatively large European source with respect to CFC-11, but not large enough to account for the mean global source. Since the U.S. and Australia appear to contribute still lesser relative amounts of CCl_4 , relative to CFC-11, we may conclude, as in the case of CFC-12, that substantial additional sources must exist in the USSR, China, Japan, or developing countries distant from ALE sites.

Future Projections of Industrial Halocarbon Production

There is a need for projections of trends in atmospheric concentrations of trace gases into the future in order to calculate possible future changes in the stratosphere. There is no bar to developing forecasts for the next hundred years, but it is doubtful whether the result is meaningful. Projections require not only a complete understanding of the processes leading to the emission of a trace species and its atmospheric fate, but also detailed economic projections which must incorporate forecasts of population and GNP changes,

Table 3-5. Relative Molar Source Strengths Derived by Prather (1985) from Cross-Covariances of ALE Data (See Text for ALE References)

	CFC-11	CFC-12	CH_3CCl_3	CCl_4	N_2O
ALE (Ireland)*	1	1.1	1.8	0.28	30-70
ALE (Oregon)	1	1.2 ± .2	2.5 ± .3	0.15 ± .05	x
ALE (Tasmania)	1	0.9 ± .2	0.9 ± .2	0.15 ± .04	x
Global Estimate (flux in Gg/yr)	1 (265)	1.76 (410)	1.94 (500)	0.34 (100)	52 (2800 of N)

* Error estimates are ± 10% for all but N_2O (see text).
 Calibration factors for the ALE data have not been applied.
 N_2O flux estimates corresponds to 0.2% per annum.
 N_2O sources are undetectable (x) at Oregon and Tasmania.

regional development, and changes in technology. (Imagine a projection for today, rendered in 1885.) For gases of solely industrial origin such as CFCs, assessment must be made of the future availability of raw materials, capital for investment, possible new technology, and external constraints such as regulations, wars, famines, and economic depressions. We believe that it is not possible to render reliable, accurate long-term forecasts of this nature.

Forecasts for CFCs 11 and 12 up to 1995 have been prepared by CEFIC (European Fluorocarbon Technical Committee (EFCTC), A CEFIC Sector Growth Halocarbon Trend Study, 1983–1995). These forecasts cover Western Europe, Australia, New Zealand and South Africa and, in a separate forecast, the rest of the world (ROW) excluding North America, Japan and Eastern Bloc countries; i.e. the forecast covers areas of the world where European CFC producers have detailed market knowledge.

Although the CEFIC forecast is not globally complete it adds some perspective to a global view of CFC 11 and 12 usage in the next decade. High growth rates for CFCs 11 and 12 seen in OECD countries in the 1960's and 70's are not expected to return, even in developing countries where current demand is small. The overall growth rate is projected to be ~1.5% per annum over the next ten years. Slightly higher growth rates in developing countries are not expected to significantly change the overall distribution of demand over the next ten years. The reliability of this forecast must be viewed in the context of recent events. Production of CFC-11 and CFC-12 by reporting companies increased 16% from 1982 to 1984 (Figure 3-6). This was a period of high economic growth in the USA and Japan, and economic stagnation in Europe, and one might speculate that growth would have been even faster if European economics were more robust. Thus world production can evidently increase very rapidly in favorable economic circumstances, in this case, five times faster than the regional CEFIC projections.

Projections are notoriously unreliable even over a short time span (less than 10 years). For example, several groups in the late 1970's made projections of the future growth of CFCs 11 and 12 in Western economies, ranging from 3–6% per year (Rand, 1980; SRI, 1982; OECD, 1983) whereas reported production for 1979–83 was in fact static (Figure 3-6). The latest Rand report (1986) estimates about 5% per year growth for CFC 11 and 2.6% per year for CFC 12 through 1990. Their estimates for long-term growth (through 2075), based on a variety of assumptions, range from 0.6–3% per year. Long term concentrations derived from these estimates span a very wide range, and any of the scenarios would appear to be feasible. It does not seem possible to single out any particular scenario as probable. Thus a range of assumptions needs to be explored in any assessment document. The resulting atmospheric conditions will span a correspondingly wide range, and a scientific assessment must concentrate on determining which part of the range presents significant environmental risks.

3.2 NITROUS OXIDE (N₂O)

3.2.1 Global Atmospheric Trend and Distributions

The mean global concentration of N₂O is about 300 ppbv, with very little geographic variation (< 1% except near source regions) (Pierotti and Rasmussen, 1977). Nitrous oxide has a long atmospheric lifetime, ~150 yrs., and large natural sources, hence atmospheric trends are expected to be small. A series of papers in the 1970's predicted important anthropogenic sources for N₂O (for example, McElroy, 1976; Crutzen and Ehhalt, 1977; McElroy *et al.*, 1977; Weiss and Craig, 1976; Pierotti and Rasmussen, 1976), and suggested possible increases for the global concentration of the gas. Weiss (1981) presented convincing evidence for a steady increase of about 0.7 ppb yr⁻¹ during the period 1977–1980, confirming these

SOURCE GASES

ideas. Although the rate of increase is indeed small ($0.2\% \text{ yr}^{-1}$), implications for the atmosphere are very significant (see below).

Recent data for N_2O from the ALE program are shown in Figure 3-7, along with trends observed at each station. The interhemispheric difference is small for N_2O (~ 1 ppb, N-S) (Weiss, 1982), but rates of increase appear to be larger in the Northern Hemisphere ($0.25\text{--}0.7\% \text{ yr}^{-1}$) than in the Southern Hemisphere ($0.1\text{--}0.2\% \text{ yr}^{-1}$). If shown to be statistically significant, this pattern would be counter to that for CFCs, indicating an increasing imbalance between northern sources and global sinks.

Recently, enhanced concentrations of N_2O have been observed in the lower atmosphere of Amazonia (Figure 3-8), a major source region as discussed below. The observed enhancement near the source is quite small, due to the large atmospheric burden of the gas. Nevertheless, this pilot study shows that considerable information about emissions from a large area can be derived from observations of geographical gradients. Measurements of temporal and spatial variations of N_2O could yield important insights into the atmospheric cycle of the gas, if the precision of routine measurements could be improved from the current value of ~ 1 ppb to about 0.1 ppb (cf. Prather, 1985). It appears possible to develop technology for this purpose (e.g. using diode inset technology), and an important contribution to atmospheric science would result.

3.2.2 Sources and Sinks

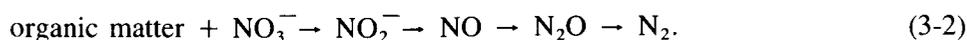
A. Natural Processes

Nitrous oxide is removed from the atmosphere mainly by photolysis in the stratosphere and secondarily by reaction with $\text{O}(^1\text{D})$.



The rate for destruction is calculated to be $10.5 (\pm 3) \times 10^6$ tons N yr^{-1} , using observed distributions (e.g. Goldan *et al.*, 1980) and calculated rates for photochemical reactions in the stratosphere. The rate of increase in the atmosphere, currently 0.7 ± 0.1 ppb yr^{-1} , corresponds to 3.5×10^6 tons N yr^{-1} . Total emissions for N_2O amount therefore to $14 \pm 3 \times 10^6$ tons N yr^{-1} . The magnitude of the annual increase, though small (0.2% per year), implies a discrepancy in excess of 30% between current sources and sinks, (see Table 3-6). Since N_2O is the dominant precursor of stratospheric odd nitrogen, we expect gradual increases in the levels of NO_x in the stratosphere, adding up eventually to at least 30% above current levels.

Nitrous oxide is an obligatory free intermediate in microbial denitrification and other dissimilatory nitrogen reduction processes (Payne, 1983),



Sequential reduction of the nitrogen atom in (3-2) provides a respiratory electron sink for a wide variety of bacteria under anaerobic conditions. Denitrification is most often observed in environments isolated

SOURCE GASES

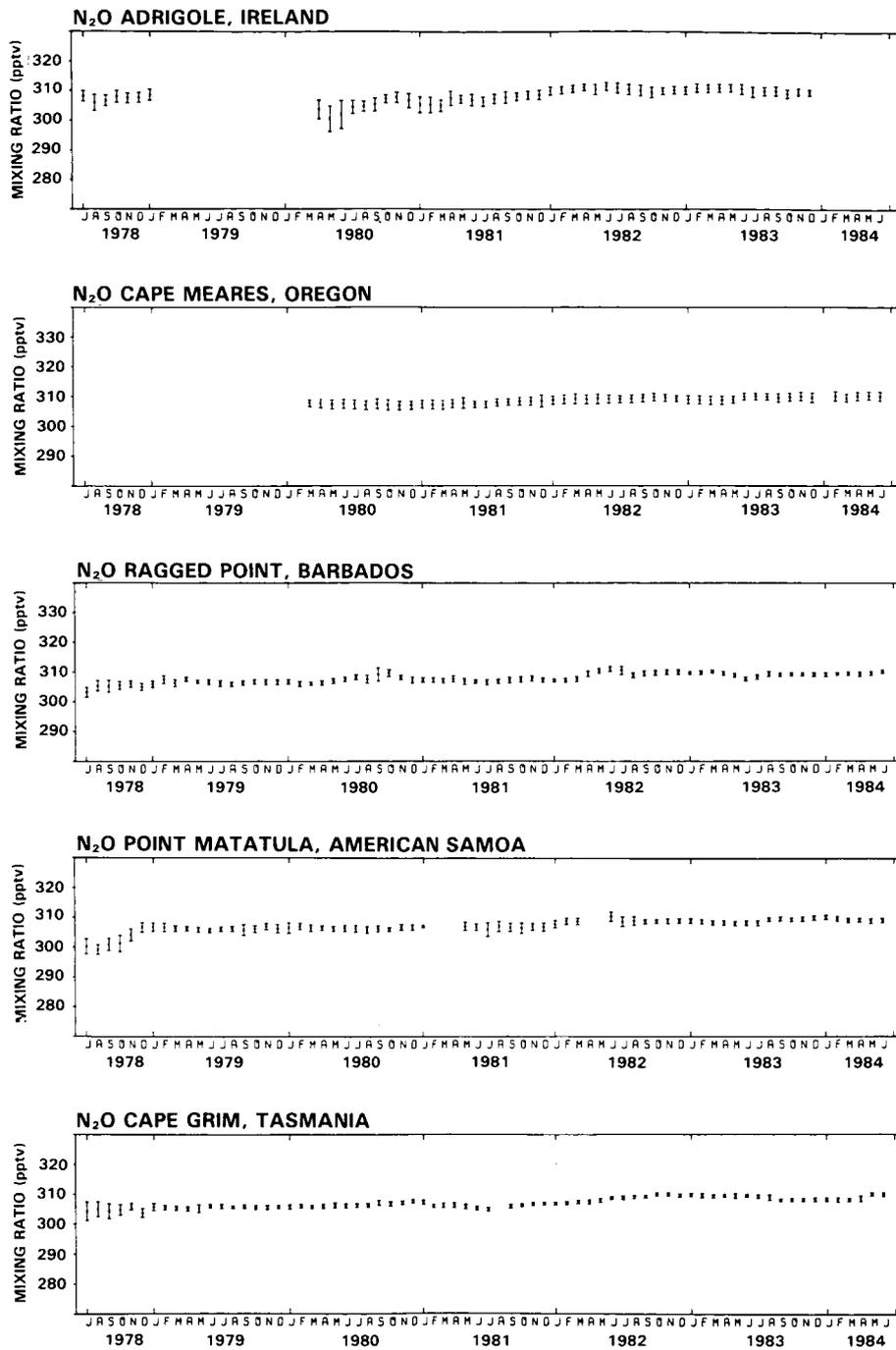


Figure 3-7. ALE/GAGE network data. As in Figure 3-1 but for N₂O measured on Porasil column with a calibration factor of 0.92 and with the 1978-1983 measured trends being 0.77, 0.27, 0.24, 0.09 and 0.18% per year at the 5 stations.

C-2

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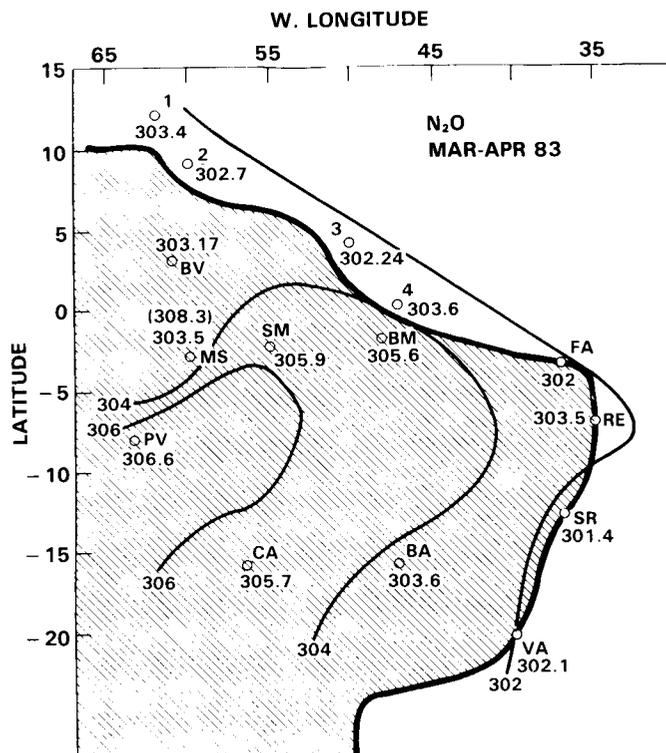
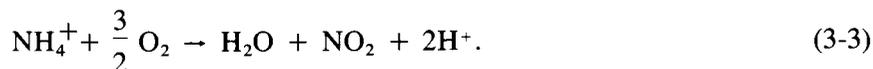


Figure 3-8. Isopleths of N₂O mixing ratio (ppbv) over Brazil, March-April 1983 (Wofsy, personal communication, 1985).

from atmospheric oxygen and supplied with abundant sources of oxidizable detrital material; organic-rich sediments, flooded soils, and closed ocean basins, for example. Such systems were thought at one time to be the principal sources for atmospheric N₂O, but this idea turned out to be incorrect. It has been observed that static anaerobic ecosystems contain typically very low concentrations of N₂O, indicating that virtually all the N₂O produced in denitrification is consumed *in situ* (Cohen and Gordon, 1978; Hashimoto *et al.*, 1983; Blackmer and Bremner, 1976; Firestone *et al.*, 1979; Firestone and Tiedje, 1979). These results reflect the ability of microorganisms to use N₂O as an oxidant in systems which are prevented from exchanging gases with the environment.

Significant quantities of N₂O are produced, however, by a variety of aerobic or partially aerobic environments, especially soils. Intense emissions are associated with rapid oxidation of organic matter or of reduced N in fertilizer (Bremner and Blackmer, 1978; Freney *et al.*, 1979; Hutchinson and Mosier, 1976; Breitenbeck *et al.*, 1980; Seiler and Conrad, 1981; Duxbury *et al.*, 1982; Slemr and Seiler, 1984; Robertson and Tiedje, 1984), and it appears primary nitrification is a major pathway for production of N₂O (Yoshida and Alexander, 1970),



Nitrification is a key step in the aerobic degradation of organic detritus. It is carried out by a small group of autotrophic bacteria, and the process yields 1-3 molecules of N₂O per 1000 nitrite molecules under fully aerobic conditions. The yield of N₂O increases dramatically under low-oxygen conditions, rising to 10% of the nitrite production rate for partial pressures of O₂ below 0.01 atm (Goreau *et al.*, 1980).

Table 3-6. Nitrous Oxide Sources and Sinks (1984 concentration 303 ppb)
(from McElroy and Wofsy, 1985)

A. <i>Atmospheric burden</i> (10^6 tons as N)	1500
B. <i>Sinks + accumulation</i> (10^6 tons N yr ⁻¹)	
stratospheric photolysis + reaction with O(¹ D)	10.5 ± 3
accumulation (0.7 ppb yr ⁻¹)	3.5 ± 0.5
total	14.0 ± 3.5
C. <i>Sources</i> (10^6 tons N yr ⁻¹)	
oceans	2 ± 1
combustion: coal + oil, 4 ± 1	
biomass, 0.7 ± 0.2	4.7 ± 1.2
fertilized agricultural lands	0.8 ± 0.4
grasslands	< 0.1
~ boreal and temperate forests	0.1 - 0.5
tropical and subtropical forests and woodlands (extrapolation of soil data)	7.4 ± 4
total	15.3 ± 6.7
D. <i>Tropical Contribution</i> (10^6 tons N yr ⁻¹)	
biomass burning	0.6
soil emissions	7.4
total	8.0

While it is clear that aerobic soils and waters are major sources of atmospheric N₂O, reductive pathways may nevertheless be important. Studies by Robertson and Tiedje (1984) showed active denitrification in aerobic soil cores from forest environments. Using an oxygen microprobe, Sexstone *et al.* (1985) showed that soil aggregates contain active, anaerobic microsites where denitrification proceeds. This direct demonstration confirms ideas held by soil scientists for many years (cf. Arnold, 1955). Hence a significant source of N₂O may be denitrification along a microscopic O₂ gradient, from which escape of N₂O may be relatively rapid. Important modification of the N₂O source may occur therefore when forests are converted to agriculture, since soil structure and organic content is radically changed. The nature of the effect on N₂O has not yet been elucidated, however.

Soils in tropical forests emit N₂O at rates far in excess of soils in most other environments, as shown by recent measurements from forest sites in the USA, Germany, Brazil, Ecuador, and elsewhere (see, for a review, Seiler and Conrad, 1985). Table 3-7 provides a summary of existing data for soils. Release rates for tropical forests average about 2×10^{10} molecules N₂O cm⁻² sec⁻¹, as compared for example, to $1-2 \times 10^9$ cm⁻² sec⁻¹ in New Hampshire (Keller *et al.*, 1983, updated for other tropical sites, 1985). It is this large source whose signature is observed over South America, although biomass burning may

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also contribute (Crutzen *et al.*, 1985, see below). Since the tropical forests of the world are being rapidly modified, this large natural source of N₂O is likely to be changing. It would be of great interest to discover in what direction these changes might go.

B. Anthropogenic Processes

Concerns arose during the 1970's (for example, McElroy *et al.*, 1977; Crutzen and Ehhalt, 1977) that use of nitrogenous fertilizer would artificially enhance biogenic emissions of N₂O, leading to increased concentrations in the atmosphere. Recent investigations indicate that fertilization with NH₄⁺ or urea does indeed stimulate emission of N₂O, although the yield is relatively small (Hutchinson and Mosier, 1976; McKenney *et al.*, 1978; Breitenbeck *et al.*, 1980; Seiler and Conrad, 1981). Between 0.1 and 0.5% of the reduced nitrogen in fertilizer is converted to N₂O within a few weeks of application, with highest efficiency for conversion at highest rates of fertilization. The ultimate release of N₂O after fertilization could be higher, however, since fixed nitrogen is likely to be assimilated into organic material and re-oxidized a number of times before it is lost eventually from the soil.

Table 3-7. Nitrous Oxide Fluxes from Soils* (Global mean value = 2×10^9 cm⁻² sec⁻¹)

1. Undisturbed soils

Mean Flux (10 ⁹ cm ⁻² sec ⁻¹)	Location	Environment	Duration	Reference
0.45, 1.0	New Hampshire	Northern Hardwood Forest	1 yr.	Keller <i>et al.</i> , 1983 Goreau, 1981
17	75 km N.E. of Manaus, Brazil	Tropical Moist Forest	8 mos., 4 dates	Keller <i>et al.</i> , 1985 Goreau and Demello, 1985
25	Puerto Rico	Subtropical Moist Forest	1 day, dry season	Keller <i>et al.</i> , 1985
5.7	Colorado	Natural Shortgrass Prairie	62 days, June	Mosier <i>et al.</i> , 1981
3.0	Louisiana	Salt, brackish and fresh marshes	2 yr.	Smith <i>et al.</i> , 1983
6.1	New York State	Northern Hardwood Forest, Mineral soil	1 yr.	Duxbury <i>et al.</i> , 1982
6.8	Florida Everglades	organic soil	1 yr.	Duxbury <i>et al.</i> , 1982

Table 3-7. Nitrous Oxide Fluxes from Soils* (Global mean value = $2 \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1}$) — Continued
2. Agricultural and disturbed soils

Mean Flux ($10^9 \text{ cm}^{-2} \text{ sec}^{-1}$)	Location	Environment	Duration	Reference
32	75 km N.E. of Manaus, Brazil	clearcut forest	8 mos.,	Keller <i>et al.</i> , 1985 Goreau and DeMello, 1985
8.2	Iowa	Soybean field	1 yr.	Bremner <i>et al.</i> , 1980
8.6	Iowa	farmland, fallow	June	Breitenbeack <i>et al.</i> , 1980
17.7	Colorado	cornfield, fertilized	growing season	Hutchinson and Mosier, 1976
2.9	California	cornfield	June, 1977	McKenney <i>et al.</i> , 1978
7.1	California	cornfield fertilized	June, 1977	McKenney <i>et al.</i> , 1978
11.2	California	tobacco field	June, 1977	McKenney <i>et al.</i> , 1978
51	California	tobacco field, fertilized	June, 1977	McKenney <i>et al.</i> , 1978
-2.7	U.K.	Field, fertilizers Perennial ryegrass	Aug.-Oct.	Ryden, 1981
430-1500	Florida Everglades	cultivated organic soils		Terry <i>et al.</i> , 1981
3.6	Canberra, Australia	clovergrass	5 mos.,	Freny <i>et al.</i> , 1979
19	New York State	alfalfa, fertilized cornfields (mineral soils)	1 yr.	Duxbury <i>et al.</i> , 1982

*Table prepared by M. Keller

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Combustion introduces another important anthropogenic source of N₂O. Pierotti and Rasmussen (1976) and Weiss and Craig (1976) observed enhanced N₂O in power plant plumes, and they measured the N₂O/CO₂ ratio from coal and oil-fired plants. They argued that combustion of coal could be the dominant anthropogenic source of N₂O. Crutzen *et al.* (1979) reported excess N₂O in smoke plumes from biomass burning. Recent kinetic studies (Perry, 1984) have shown that N₂O is produced in flames from fuel nitrogen by the rapid reaction,



Note that the NCO molecule is also the precursor for much of the NO_x from combustion, by reactions with O₂ or O, and one might therefore expect a relationship between emissions of N₂O and NO_x. A recent investigation by W.M. Hao (Harvard University, Ph.D. thesis, 1985) confirms such a relationship in commercial power plant emissions and supports the views of Weiss and Craig, and of Pierotti and Rasmussen on the potential importance of coal-fired plants, since coal is a fuel rich in organic nitrogen. A preliminary report on N₂O from biomass burning (Crutzen *et al.*, 1979) indicated very high emissions of N₂O, but the same authors lowered their estimate by a factor of 10 in a recent article (Delany *et al.*, 1985a). Emissions from biomass burning now appear to be consistent with the nitrogen content of the fuel.

Table 3-6 summarizes current understanding of sources for atmospheric N₂O (from McElroy and Wofsy, 1985). Estimates for the marine source are based on the nitrification process (Elkins *et al.*, 1978; Cohen and Gordon, 1979) using observations of accumulation of N₂O and depletion of O₂ in marine waters, supported by extensive data showing small mean supersaturations for N₂O dissolved in surface waters of the world's oceans (R. Weiss, private communication, 1983). The value for combustion is derived from the data discussed above, scaled to NO_x emissions data from fossil fuel combustion and biomass burning (Seiler and Crutzen, 1980; Hao, 1985). The entry for fertilized agricultural lands assumes application of chemical fertilizer at the rate of 40 × 10⁶ tons N yr⁻¹ and a similar rate for use of manures, with an overall yield for N₂O of 1 ± 0.5%, based on the soil studies cited above. The value for forests reflects an average of measurements of forest soils in Europe, the USA, Puerto Rico, Ecuador and Brazil.

3.2.3 Discussion

It appears that anthropogenic processes account for about one third of current emissions. The table (3-6) implies a pre-industrial concentration of N₂O (245-275 ppb) approximately 10-20% lower than today (304 ppb). Weiss (1981) has interpreted his atmospheric N₂O data, including unpublished results for the period 1961-78, to estimate a slightly higher preindustrial N₂O level, in the range 280-290 ppbv. Future studies of air bubbles in polar ice cores should eventually provide a history of atmospheric N₂O for the period before the modern era of measurements. Preliminary data presented by Pearman *et al.* (1985) indicate an increase of 25 ppb from 1600 AD to the present.

The global N₂O abundance is evidently lower than the steady-state value for current emissions. If the present pattern of emissions persisted, the abundance of atmospheric N₂O would grow slowly to about 400 ppb. Khalil and Rasmussen (1983b) have estimated that atmospheric N₂O will reach 380 ppbv about 50 years from now; likewise Ramanathan *et al.* (1985) estimated N₂O levels of 375 ppbv by the 2030. However, there is little reason to project that emissions should remain constant in the future. Sources associated with combustion and with intensive agriculture are likely to increase, and we might expect temporarily increased fluxes of N₂O from tropical forests disturbed by exploitation. On the other hand, the source from crop land and pasture may be smaller than from undisturbed systems. A much improved understanding is needed to predict future emissions of N₂O and studies of tropical forests and industrial and agricultural sources are clearly important to this aim.

3.3 OXIDES OF NITROGEN

3.3.1 Distribution and Trends

Oxides of nitrogen in the troposphere have an important, though indirect influence on the stratosphere by interacting with the chemistry of tropospheric radicals (i.e. OH) and by influencing biological activity in important ecosystems. The lifetime of odd nitrogen in the troposphere is short (1-7 days) and sources are geographically concentrated. Sinks are also variable in time and space; removal mechanisms are associated in part with photochemical activity and in part with wet and dry deposition. Hence ambient concentrations fluctuate over a wide range. The global distribution is highly complex, and poorly determined, and there is no direct information about trends. It may be inferred, however, that concentrations have probably increased substantially in important regions of the atmosphere (see below) due to anthropogenic activity.

Lowest concentrations of NO_x are found in the remote marine boundary layer, e.g. the central Pacific Ocean where NO mole fractions are only a few parts per trillion (McFarland *et al.*, 1979) and total NO_x ($=\text{NO} + \text{NO}_2$) may be inferred to be 10-15 ppt. Measurements of NO_2 by Noxon (1983) at 3 km in the same region indicate somewhat higher concentrations of this gas, ≈ 30 pptv. Levels of NO appear to increase in the upper troposphere, up to 50 pptv (Kley *et al.*, 1981; Carroll and Ridley, 1984; Torres, 1984; Bradshaw *et al.*, 1984) indicating a downward flux of this material to the subtropical ocean. This inverted gradient may reflect transport from the stratosphere, or from lightning or land sources in tropical convergence regions, with the NO_x -rich air in this case carried aloft by deep convection and deposited in the upper troposphere.

Data for NO_x in continental areas indicate higher concentrations than in marine areas, especially over populated lands. Nitric oxide concentrations in the middle troposphere vary from as low as a few ppt to more than 200 ppt, and levels may exceed 1000 ppt in the lower atmosphere at times (see reviews by Logan, 1983; Dickerson, 1984; Drummond *et al.*, 1985). Data for Niwot Ridge, Colorado, show an enormous range of concentrations for NO_x , as this rural site is influenced at times by urban pollution, while at other times it receives air transported from the very clean marine middle troposphere (Bollinger *et al.*, 1984). The Niwot Ridge data also show that organonitrates and peroxy nitrates may be very important in the tropospheric cycle of odd nitrogen (Singh *et al.*, 1985).

3.3.2 Sources and Sinks

The focus of the present review is the influence of tropospheric NO_x on lifetimes for stratospheric source molecules (CH_3CCl_3 , CH_3Cl , CH_4) through interactions with tropospheric photochemistry. It would be of great interest to know whether global tropospheric NO_x levels are perturbed by human activities. Since direct information on trends is lacking, we must fall back on analysis of sources for NO_x .

Combustion Sources

The emission rate for fixed N from combustion of fossil fuels, $\sim 20 \text{ Tg yr}^{-1}$, may be assessed with some confidence using emission factors for NO_x and statistics for fuel use (see, for example, Logan, 1983 or Ehhalt and Drummond, 1982). Emissions in the U.S. doubled between 1950 and 1970, but have been relatively constant in the last decade due to levelling off of overall energy use (EPA, 1984). The impact of this NO_x on global tropospheric chemistry remains uncertain, however, because a significant fraction of NO_x from industrial emissions may be removed near the source. A number of papers have suggested that industrial emissions of NO_x are responsible for increasing the concentrations of OH and O_3 in the

SOURCE GASES

Northern Hemisphere (Crutzen, 1973; 1979; Chameides and Walker, 1973; Fishman *et al.*, 1979; Seiler and Fishman, 1981). Unfortunately, knowledge of the processes which disperse NO_x from industrial sources is inadequate for reliable assessment of this phenomenon. Note that, as mentioned above, combustion of relatively high-N, unrefined fuels (coal, agricultural residuals, residual oil) produce NO and N_2O largely through related chemical pathways involving NCO generated during fuel pyrolysis.

Fuel N is likely to be the major source of NO emitted from biomass burning since temperatures are thought to be too low for fixation of atmospheric N_2 . Two independent studies suggest that the amount of biomass fuel burned annually is $\sim 7 \times 10^{15}$ gm yr^{-1} , or $\sim 3 \times 10^{15}$ gm C yr^{-1} (Seiler and Crutzen, 1980; Logan *et al.*, 1981), mostly in tropical regions. Logan (1983) used these assessments, in combination with data for the nitrogen content of vegetation and experimental determination of the conversion efficiency of fuel N to NO_x , to estimate that the source of NO_x from biomass burning could be as large as 12 tg N yr^{-1} . Delany *et al.* (1985a) recently reported measurements of NO_x in the polluted boundary layer in the vicinity of biomass fires. Their observed ratio of $\Delta\text{NO}_x/\Delta\text{CO}_2 = 1.9 \pm 0.3 \times 10^{-3}$ may be used to estimate a global source of NO_x , ~ 7 tg N yr^{-1} , basically in agreement with earlier estimates.

Emissions from biomass burning are spatially and temporally concentrated, making the assessment of impacts on global chemistry difficult. In this respect, the problem is similar to that for urban emissions. The regions directly affected by fire plumes are too small to influence the global lifetimes of CH_4 or CH_3CCl_3 , for example. However, if a substantial fraction of this NO_x escapes to distant parts of the tropical troposphere, the lifetimes of these species could be significantly shortened, due to enhanced concentrations of OH, with potentially important consequences for stratospheric chemistry (Delaney *et al.*, 1985a).

Natural Sources

Natural sources for NO_x include microbial activity in soils, lightning, and oxidation of stratospheric N_2O . The stratospheric source is only about 0.5 tg N yr^{-1} over the whole globe; while this is much smaller than the other sources discussed here, it is likely very important in the chemistry of the upper troposphere, especially in marine locations with negligible sources near the ground (Levy *et al.*, 1980).

There is no doubt that lightning produces NO_x in the atmosphere (Noxon, 1978b; Liu *et al.*, 1983), but there has been considerable dispute about the magnitude of the source. Most current estimates are < 10 tg N yr^{-1} (Tuck, 1976; Chameides *et al.*, 1977; Dawson, 1980; Jackman *et al.*, 1980; Borucki and Chameides, 1984), and values significantly higher than this are inconsistent with the deposition rate of nitrate in precipitation (Logan, 1983; Ehhalt and Drummond, 1982; Borucki and Chameides, 1984). Lightning may provide the major source of NO_x in the middle and upper troposphere in the tropics (Liu *et al.*, 1983), and may even be important as a source of NO_x in the lower stratosphere (Ko *et al.*, 1985).

Odd nitrogen emissions from soils have attracted interest rather recently (Galbally and Roy, 1978; Galbally, 1985). A summary of available data is given in Table 3-8. Soils may either emit or consume NO and NO_2 . A net positive flux of NO is the rule on average, except where NO levels in the air are very large (> 1 ppb), while on average most soils consume NO_2 (for a review, see Galbally, 1985). The global source of NO from soils may be roughly estimated as ~ 10 – 15 tg N yr^{-1} , a very significant contribution. Particular interest attaches to large emission rates observed from intensive agriculture and livestock operations, and from tropical forest soils. Both of these contribute NO_x to the atmosphere in areas distant from industrial sources, and both are being modified globally by human activities (increasing agriculture, declining areas of tropical forest). Noteworthy is the association between high emission rates for N_2O and for NO, which may derive from the fact that most biological processes producing one gas also produce the other (e.g., nitrification, Lipschultz *et al.*, 1981; denitrification, Payne, 1983).

Table 3-8. Measurements of NO Emissions from Soils

	Flux kg N m ⁻² sec ⁻¹	References
Ungrazed pasture (average)	1.6 × 10 ⁻¹²	Galbally and Roy, 1978
Grazed pasture (average)	3.5 × 10 ⁻¹²	
Grazed pasture (range)	1–50 × 10 ⁻¹²	Galbally and Roy, 1981
Fertilized grass (weighted annual average)	1.9 × 10 ⁻¹²	Johansson and Granat, 1984
Unfertilized barley (weighted annual average)	0.6 × 10 ⁻¹²	
Croplands (range)	0.1–62 × 10 ⁻¹²	
Unfertilized forest soil (median) (range)	0.3 × 10 ⁻¹² 0.1–0.8 × 10 ⁻¹²	Johansson, 1984
Bare, unfertilized soil, Finthen (average) (range)	2.2 × 10 ⁻¹² –5.8 to 14.2 × 10 ⁻¹²	Slemr and Seiler, 1984
Bare, unfertilized soil, Utrera (range)	–2.2 to 107 × 10 ⁻¹²	
Crested wheat grass (daily mean) (range)	7 × 10 ⁻¹² –9.3 to 28.0 × 10 ⁻¹²	Delany <i>et al.</i> , 1985
Amazon Tropical Forest	10 × 10 ⁻¹²	NASA/ABLE II (W. Kaplan <i>et al.</i> , 1985)

Note: 1 × 10⁻¹² kg N m⁻² sec⁻¹ = 4.3 × 10⁹ molecules cm⁻² sec⁻¹

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3.3.3 Discussion

The stratosphere will be indirectly affected by future changes in global levels of tropospheric NO_x . Many industrial, agricultural and natural sources of NO_x are closely associated with analogous production processes for N_2O . Automobiles and lightning are perhaps the principal exceptions. The observed imbalance ($\sim 30\%$) between current sources and sinks for N_2O implies associated large increases in global emissions for both N_2O and NO_x . Unfortunately, it is not clear to what extent NO_x from industrial emissions, automobiles, or biomass burning affect remote regions of the atmosphere, and consequently the magnitude of the global influence of anthropogenic activities remains unclear. Resolution of this important issue requires careful experimental and theoretical investigation of transformations and transports of nitrogen oxides from industrial source areas and biomass burning areas to the global troposphere, as described for example in the recent Workshop Report from the proposed Global Tropospheric Chemistry Program. The expected sign of the effect for NO_x is clear, however: global levels of NO_x are almost certainly higher today than in preindustrial times. Global levels of OH could be either higher or lower, however, since increasing production of OH due to NO_x must be offset in part by anthropogenic CO (Wofsy, 1976; Sze, 1977; Chameides, *et al.*, 1977)(see below), which enhances the sink for OH; emissions of hydrocarbons may have an effect also. There is evidently a strong need for much better definition of the sources, sinks, and atmospheric cycles for NO_x .

3.4 METHANE (CH_4)

3.4.1 Distributions and Trends

Atmospheric measurements using GC/FID techniques, taken since 1965, have now clearly established that the concentration of methane is increasing (Rasmussen and Khalil, 1981b; Blake *et al.*, 1982; Fraser *et al.*, 1981, 1983, 1984; Khalil and Rasmussen, 1982, 1983b, 1984; Ehhalt *et al.*, 1983). Data have been obtained from at least six primary sites between 1979 and the present, including continuous measurements at Cape Meares, Oregon (Khalil and Rasmussen, 1983c). Methane concentrations have increased at every site consistent with the record from Cape Meares (see Figure 3-9). The record shows interannual variability in the trend of CH_4 and there is evidence that recent variability is associated with the El Niño-Southern Oscillation (ENSO) phenomenon (Khalil and Rasmussen, 1985f). During the recent ENSO event (1982-83), concentrations of CH_4 fell well below levels extrapolated from previous years (1978-81) and recovered with a rapid increase afterwards (Figure 3-9, 3-10), similar to behavior observed for CO_2 (Gammon and Komhyr, 1983; Gammon *et al.*, 1984). The occurrence of this major El Niño reduced the estimated global long-term increase of CH_4 to an average of about 1% per year for the period 1979-1984, whereas data from 1979-1982 had suggested a more rapid increase of about 1.8% yr^{-1} . Analysis of air trapped in polar ice (Craig and Chou, 1982; Rasmussen and Khalil, 1984b) shows that CH_4 levels in the atmosphere have been increasing for several centuries, and have roughly doubled from values near 0.7 ppm that prevailed for thousands of years prior to the increase recorded in recent times. Analysis of Migeotte's plates by Rinsland *et al.* (1985a) indicates 1.14 ppm in Europe in 1951, with recent plates giving 1.58 ppm in 1981, corresponding to 1.1% mean annual increase over 30 yrs.

Seasonal cycles have been documented at various latitudes generally showing lowest concentrations in late summer and highest concentrations in winter and spring. At high northern latitudes there is a strong rise of CH_4 during fall, probably caused by a seasonal peak of emissions from water-saturated soils that are frozen much of the year. Other features of the CH_4 seasonality are generally consistent with the calculated seasonal cycles of OH. As with CO and CO_2 , the amplitude of the seasonal cycle is largest at high northern latitudes and diminishes towards the equator (Khalil and Rasmussen, 1983c; Fraser *et al.*, 1983b).

The detailed global distribution and seasonal variation of CH_4 has been recently synthesized from several thousand air samples collected by the global flask network operated by GMCC/NOAA, in a cooperative program with the Oregon Graduate Center and CSIRO (Australia) (Steele *et al.*, 1985, Figure 3-11). Weekly sample pairs from 17 sites allow the construction of a zonally averaged concentration surface, with a grid resolution of two weeks in time and 10° in latitude, for the two-year period 5/83-4/85. A remarkable feature of the concentration surface is the simple annual cycle of nearly constant seasonal amplitude and phase from southern mid-latitudes to the South Pole with a mid-summer minimum and fall and late-winter maxima. There is more complex seasonality at mid-to-high northern latitudes. The amplitude of the seasonal cycle increases poleward from the equator (arrow in Figure 3-11) in both hemispheres, and is highest in the Arctic. Neither the interannual variability of the local seasonality nor the latitude dependence of the secular increase can yet be recovered from the initial 24-month record. Annual mean CH_4 concentrations as a function of latitude for 1984 are shown in Figure 3-12 (Steele *et al.*, 1985). In the future, coordinated interpretations of the seasonality and distributions of the carbon-cycle trace gases (CO_2 , CO , CH_4) should greatly clarify the role of regionally important sources (e.g. tropical biomass burning, tundra metabolism). Examination of isotopic data may also prove useful in this regard (see below).

3.4.2 Sources and Sinks

We now review present knowledge of the sinks and sources of atmospheric CH_4 in order to lay the foundation for an analysis of the factors which may be responsible for the atmospheric trends. Summary tables give recent assessments of sinks (Table 3-9; McElroy and Wofsy, 1985) and sources (Tables 3-10 and 3-11; Seiler, 1984; Ehhalt and Schmidt, 1978; Khalil and Rasmussen, 1983c). As we shall see, the total sink is relatively well-known ($\pm 35\%$) but apportionment among sources is highly uncertain.

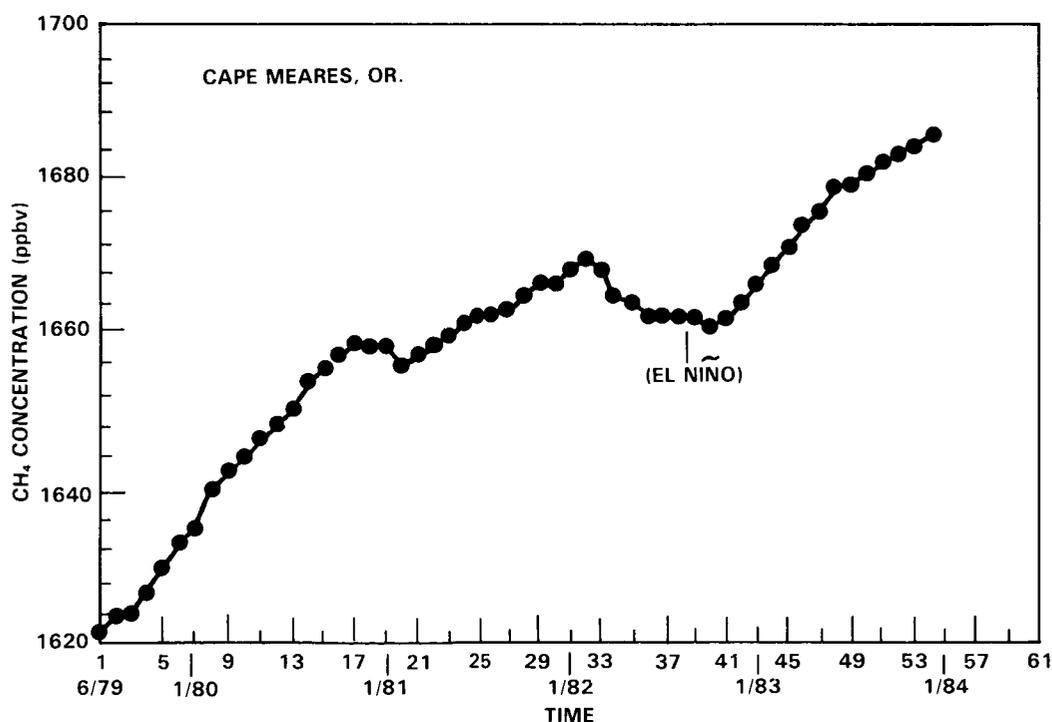


Figure 3-9. Trend of atmospheric CH_4 concentration (ppbv) measured at Cape Meares, Oregon (45°N) for the period 6/79-1/84 (Khalil and Rasmussen, JGR, 1983 updated through 1984). Seasonal variation removed by 12-month running mean, interannual variations (El Nino, 1982/83) apparent.

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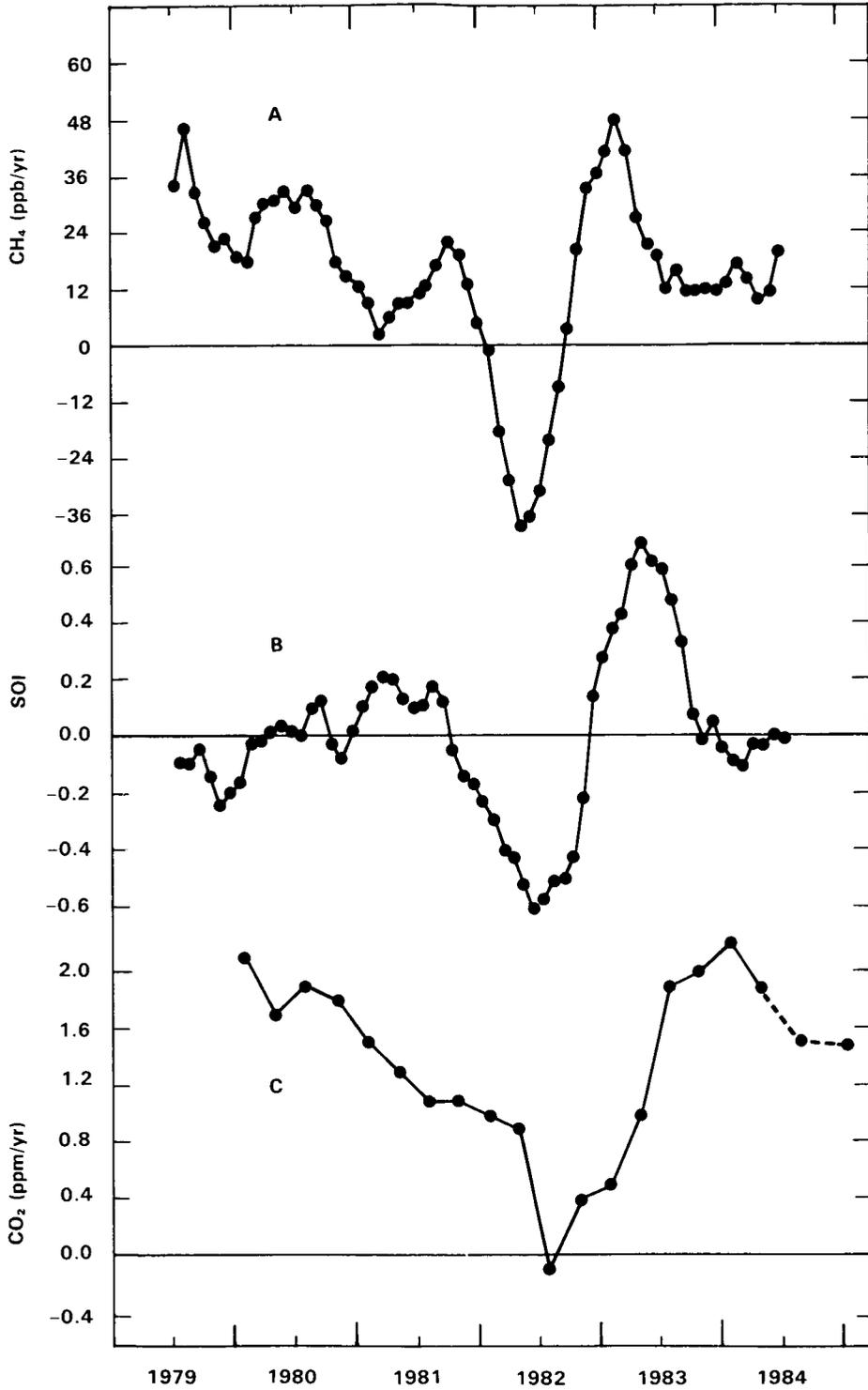


Figure 3-10. (Khalil and Rasmussen, 1985f) (a) Growth rate of atmospheric methane in ppbv/yr observed at Cape Meares, Oregon for successive 12-month overlapping intervals; (b) time derivative of the southern oscillation index (SOI) treated as in (a); (c) globally averaged year-to-year change in atmospheric CO_2 by season, plotted in forward year (Gammon *et al.*, 1985b).

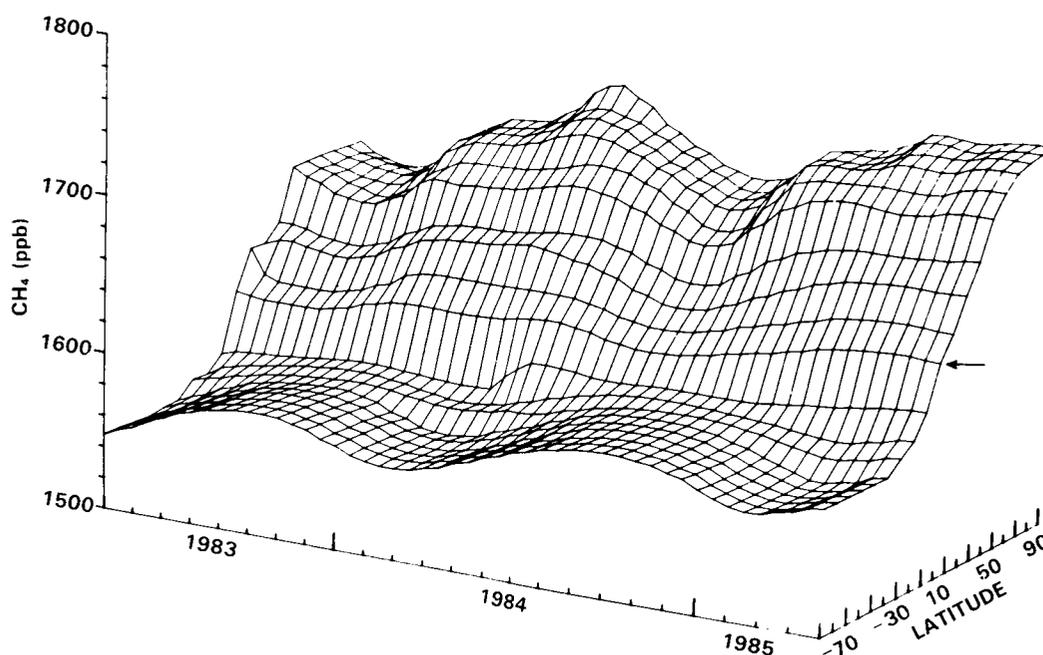


Figure 3-11. Zonally averaged global distribution of CH_4 in the lower troposphere for the two-year period 5/83-4/85. Surface constructed from biweekly flask samples from 17 sites of the GMCC/OGC/CSIRO global network, 76°N to 90°S (Steele *et al.*, 1985). Arrow indicates equator, resolution is 10° in latitude, 14 days in time.

Methane Sinks

The documented sinks for CH_4 in the atmosphere are reactions with OH (Levy, 1971) and consumption by aerobic soils (Keller *et al.*, 1983; Seiler, 1984). The temperature dependence of the reaction rate for $\text{OH} + \text{CH}_4$ (products) is not very different from that of the analogous reaction, $\text{OH} + \text{CH}_3\text{CCl}_3 \rightarrow$ (products). Hence the experimental value for the lifetime of CH_3CCl_3 , $6.5 (+3/-2)$ years from the ALE experiment (Prinn *et al.*, 1983a), provides an important constraint on the total removal rate for CH_4 from the atmosphere. An updated version of the photochemical model by Logan *et al.* (1981), which gives a lifetime for CH_3CCl_3 of ≈ 5.5 years, was used to derive the magnitude of the methane sink given in Table 3-9, $425 \pm 125 \text{ Tg CH}_4$ per year. This value corresponds to a lifetime of 11 years.

Most unsaturated soils are sinks for atmospheric CH_4 . Consumption rates in the dry subtropical areas studied by Seiler *et al.* (1984c) appear to be larger than in the wetter temperate and tropical forests studied by Keller *et al.* (1983). The value of $10 \text{ Tg CH}_4 \text{ yr}^{-1}$ for the global sink in soils was derived assuming an average deposition of 10^{10} molecules $\text{cm}^{-2} \text{ sec}^{-1}$ over $2/3$ of the earth's land area. The magnitude of this sink is evidently uncertain, but it seems unlikely to be of major importance in the global budget. According to the estimates in Table 3-9, soils remove much less than the annual accumulation of CH_4 (65 Tg yr^{-1}).

Consideration of CH_4 sinks appears to constrain the annual emissions to be $500 \pm 145 \text{ Tg CH}_4 \text{ yr}^{-1}$. This is probably one of the better-known quantities in the global CH_4 budget, as it is tied to the empirical determination of the lifetime for CH_3CCl_3 .

SOURCE GASES

Table 3-9. Methane Sinks (from McElroy and Wofsy, 1985) (1984 concentration 1630 ppb)

A. <i>Atmospheric burden</i> (4700×10^6 tons CH ₄)	
B. <i>Sinks + atmospheric accumulation</i> (tg CH ₄ yr ⁻¹)	
Reaction with OH	425 ± 125
Uptake by dry soils	10 ± 5
Accumulation (20 ppb/yr)	60 ± 15
total	495 ± 145

Table 3-10. Total CH₄ Emission into the Troposphere (Tg of CH₄ per year) (Seiler, 1984)

Source	1950	1960	1970	1980
Biogenic production	86-181	100-208	114-228	122-237
Abiogenic production	64-98	78-118	94-140	103-158
Total CH ₄ production	146-285	178-336	208-368	225-395
Average CH ₄ production	216	257	288	310
Biogenic/total (%)	62	60	59	58
Sinks				
Reactions with OH	210	230	270	290
Flux with stratosphere	44	48	56	60
Microorganisms	15	16	19	20
Total	269	294	345	370

Atmospheric Methane from Natural Sources

Natural sources for atmospheric CH₄ are wetlands (including wet tundra and sedge, floodplains, peatlands, and associated open water areas), termites, wild fires, and enteric fermentation in wild ruminants. Estimates of these sources are uncertain (see below), but natural sources may be equivalent to approximately 5-35 percent of total annual production.

Table 3-11. Methane Sources (10^{12} gm yr⁻¹) (multiply by 0.75 to obtain g C/yr)

	I	II
Enteric fermentation (cattle, sheep, etc.)	100 - 200	100 - 150
Rice paddies	~280	100 ± 50
Wetlands	90 - 300	150 ± 50
Biomass burning	—	10 - 60
Fresh water lakes	1 - 25	—
Oceans	1 - 17	—
Tundra	0.3 - 3	—
Anthropogenic/fossil fuel	16 - 50	
Other	—	10 - 150
Total	586 - 825	390 - 765

Column I is taken from Ehhalt (1974) and Ehhalt and Schmidt (1978).

Column II is taken from Khalil and Rasmussen (1983).

The CH₄ flux from any wetland ecosystem can be influenced by a range of variables including the quantity and composition of the organic substrates being decomposed, soil moisture, soil temperature, and the types of vegetation present (e.g., see Baker-Blocker *et al.*, 1977; Dacey and Klug, 1979; Cicerone and Shetter, 1981; Harries *et al.*, 1982; Seiler *et al.*, 1984a,c). An important factor is the potential for oxidation of CH₄ in the source ecosystem before release to the atmosphere.

Currently there are only a few detailed studies of specific freshwater wetland ecosystems, for example in Michigan (Baker-Blocker *et al.*, 1977) and Virginia (Harries *et al.*, 1982). The studies in Michigan measured CH₄ efflux due to bubbling only, which may underestimate the CH₄ flux, since loss by diffusive processes and through (or along) stems of plants can also be important (Dacey and Klug, 1979; Cicerone and Shetter, 1981). The Virginia swamp that was studied had been highly modified by human land management practices (e.g. drainage and timber harvest). Thus published data on annual CH₄ emissions from major freshwater wetland ecosystems is very limited. Marine wetlands have been studied in more detail, but are not a major source of atmospheric CH₄ (Bartlett *et al.*, 1985) due to the inhibiting influence of high levels of SO₄²⁻ in seawater.

The estimates for areal extent of global freshwater wetlands (see Table 3-12) are also uncertain. A generalized map of global wetland distribution is given in Figure 3-13 (Mathews, *et al.* 1986); estimated

SOURCE GASES

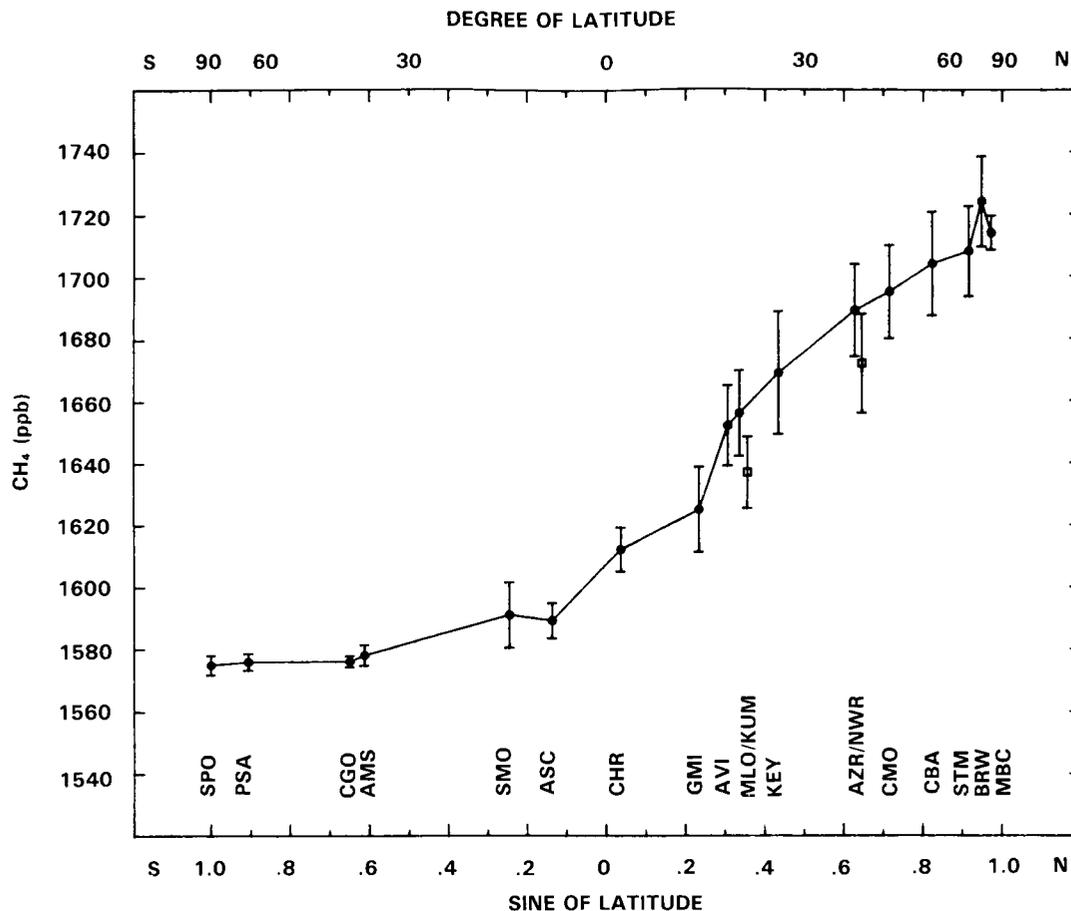


Figure 3-12. Latitudinal distribution of annual mean CH₄ concentration at 19 sampling sites from 76°N to 90°S (Steele *et al.*, 1985). The error bars reflect the relative noisiness of each site after seasonal and secular terms have been removed. High altitude sites MLO (Mauna Loa, Hawaii) and NWR (Niwot Ridge, Colorado) have lower mean CH₄ values than sea-level sites at the same latitude.

Table 3-12. Estimated Areas of Global Wetlands

Wetland areas (10³ km²) by latitudinal zones (Mathews *et al.*, 1986). Natural wetlands include wet arctic meadows, mossy bogs, seasonally and permanently inundated grasslands, woodlands, shrublands and forests; irrigated rice is self explanatory.

	90°N-30°N	30°N-30°S	30°S-90°S	TOTAL
Natural wetlands	2932	1482	21	4435
Irrigated rice	276	1240	0	1516
TOTAL	3208	2722	21	5951

regional wetland areas are given in Table 3-12. Because wetlands are generally a small percentage of total land area in any region and are of low commercial interest they receive low priority for mapping.

A strategy for improving estimates of the global flux of CH_4 from natural wetland ecosystems is urgently needed. The complex interplay of factors which influence CH_4 emissions make a global budget uncertain, and estimates of the factors underlying global change from natural wetlands are based mostly on speculation. Studies are currently underway in a few major wetlands of North America which demonstrate how the combined use of *in situ* CH_4 flux determinations and remote sensing of wetland areas and habitat distributions may produce quantitative, large-scale, long-term efflux data needed to make accurate global estimates. Such studies constitute a first step in the assessment of the causes of global CH_4 changes. For example, Table 3-13 illustrates how measured values of net CH_4 flux to the atmosphere from specific habitats in the Shark River area of the Florida Everglades are combined with Landsat-derived estimates of habitat area to derive a total flux of CH_4 to the atmosphere. The table illustrates in this case the importance of identifying the extent of the sawgrass biome and the need to distinguish it from related landforms. (R. Harriss, personal communication, 1985).



Figure 3-13. World-wide distribution of natural wetlands (Mathews *et al.*, 1986).

SOURCE GASES

The Shark River region is similar to other major seasonally flooded grasslands of the world such as the Pantanal region of Brazil and the Beni region of Bolivia, and one could extend the techniques to such areas with suitable international collaboration. Particular emphasis should be given also to the northern peatlands and tundra and to tropical floodplains and swamps, the major natural wetlands of the world. Coordination between remote sensing and *in situ* sampling is essential for such studies (see NAS, 1984).

Termites have been identified as a potentially important natural source of CH₄ (Zimmerman *et al.*, 1982). Many factors related to biology, ecology, and population of termites complicate the process of deriving an estimate for the associated global source of atmospheric CH₄ (Rasmussen and Khalil, 1983c; Khalil and Rasmussen, 1983d; Greenberg and Zimmerman, 1984). Systematic studies are now in progress which should reduce the uncertainty in emission factors for the major groups of termites, but there still remains the intractable problem of obtaining census data on termites of the world. Recent papers (Seiler *et al.*, 1984c; Rasmussen and Khalil, 1983c) argue that the global contribution of termites is smaller than projected by Zimmerman *et al.* (1982) but a lively controversy persists.

Methane Sources in Agricultural Systems

Two major agricultural sources of atmospheric methane appear to be rice paddies and cattle. These sources were identified as early as 1963 and 1948, respectively. Globally significant amounts of carbon flow through these living systems under strongly reducing conditions. In rice agriculture, rich soils are covered with water during the growing season and become anoxic: O₂, Fe⁺⁺⁺, NO₃⁻ and SO₄⁻ are depleted in sequence, after which microbial methanogenesis accelerates. In cattle and sheep digestion, specialized microbes flourish in a reducing environment and methanogenesis occurs in the final stages of a long process of breaking down complex organic material. The methane is released in the breath of these animals and by eructation and flatulence. There is little opportunity for methane-oxidizing bacteria to decompose methane produced in the rumen of cattle and sheep, but oxidation *in situ* might be significant in rice paddies under some conditions.

Tables 3-10 and 3-11 give estimates of global methane release rates from enteric fermentation in cattle and sheep and from rice paddies. The 280 tg/year figure for rice is from Ehhalt (1974), based on measurements from laboratory incubations of paddy soils by Koyama (1964). Koyama extrapolated to global rice-growing areas and temperatures, and Ehhalt later scaled upward the estimate of areas under cultivation.

Figure 3-14 shows data on worldwide rice production and area harvested for 1940-1981. Multiple cropping of many areas of the Orient has permitted production to grow faster than area under cultivation. By holding paddy soils under water for two or three growing seasons annually instead of one, increased methanogenesis from these areas is guaranteed. If one were to extend Ehhalt's 1974 estimate to 1985, one would arrive at an annual release of over 300 tg CH₄/year (225 tg C/yr.) from the world's rice paddies to the atmosphere. This estimate appears to be too large to be accommodated by the values adopted for the loss of CH₄ in Table 3-9, in combination with other source estimates.

In the past four years, new information has become available on CH₄ release from rice agriculture based on direct field studies. These support lower methane emissions than the Koyama laboratory studies, but they also point to complexities that challenge simple extrapolations. For example, Cicerone and Shetter (1981) reported field experiments in a California rice paddy from which they extrapolated a global source of only 60 tg CH₄/year, about one-fourth the early values. They showed that the dominant transport mechanism moved methane from the soil to the atmosphere not by diffusion through the water or by rising

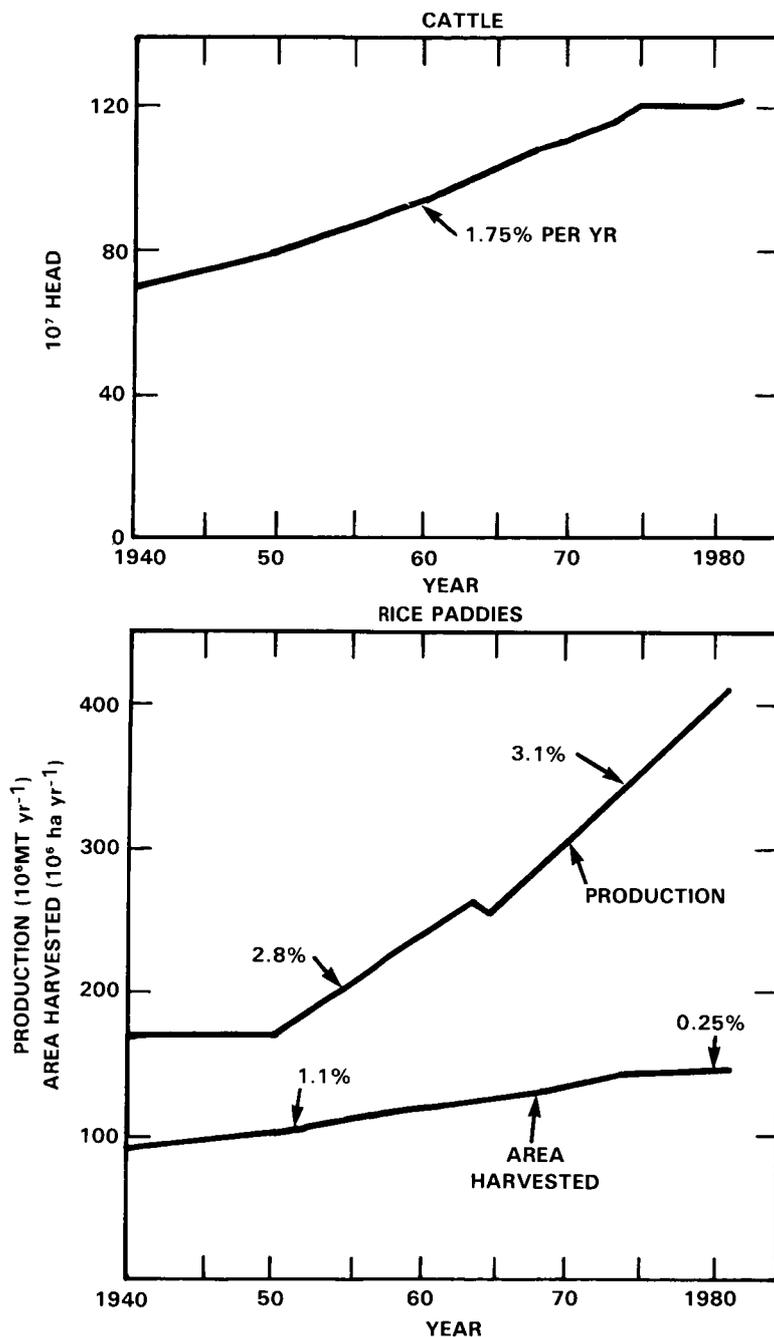


Figure 3-14. Temporal changes in the number of cattle in the world, and in the global production and area harvested of rice, taken from the United Nations FAO Production Yearbooks.

bubbles, but through (or along) the plant stems. Similar mechanisms were observed previously in littoral water litter (Dacy and Klug, 1979). Cicerone and Shetter also reported an apparent influence of nitrogen-fertilizer on methane release rates. A full-season experiment on rice emissions of methane was reported by Cicerone *et al.* (1983), indicating strong intraseasonal variation, with by far the largest fluxes occurring at the end of the growing season. The seasonally averaged methane flux, 0.25 g/m²/day, was higher than given by Cicerone and Shetter (1981).

SOURCE GASES

In 1983 Seiler *et al.* (1984a) performed an extensive season-long experiment in Spanish rice fields. They found a less pronounced intraseasonal variation than that mentioned above, an average release rate of only 0.1 g CH₄/m²/day and they confirm the role of gas transport by rice plants and found no influence of different nitrogen-fertilizer amounts. They sought and found a direct correlation between measured fluxes and soil temperatures and they derived a lower estimate for global fluxes from rice paddies, (35–59) tg CH₄/year. Subsequently, Holzapfel-Pschorn and Seiler (Seiler *et al.*, 1985a) presented new field measurements from Italian rice paddies, indicating emission rates about four times larger than found in Spain by Seiler *et al.* (1984a). These data led Holzapfel-Pschorn and Seiler to propose revised estimates of methane fluxes from rice paddies: (70–170) tg CH₄/year for 1984 and (39–94) tg CH₄/year for year 1940. The oscillation of these recent global estimates indicates the need for a much improved understanding of methanogenesis and methane release in major rice-growing agricultural systems.

Methane emissions from cows and sheep have not been the subject of much recent research, except for conventional feeding experiments designed to evaluate the efficiency of milk production in US agricultural practice. Although entire books on this subject are available (e.g. Hungate, 1960) there is probably large uncertainty in the estimated global source. For example, the full impact of varying diet, grazing conditions, animal health and nutrition and enteric microbial ecology, should be investigated further. Special attention is needed on CH₄ emissions from cattle (including goats and sheep) in Africa, India and other relatively impoverished areas. We are not aware of any studies at all on such animals.

3.4.3 Discussion

The apparent doubling of CH₄ in historic times presents a serious challenge to stratospheric research. It is clear that concentrations of stratospheric CH₄, H₂O and H₂ must have been lower for centuries prior to ~1600 AD, and stratospheric photochemistry and ozone levels must have been different. Likewise, future levels of stratospheric ozone depend sensitively on future levels of CH₄. Since we cannot quantitatively explain the current rise in CH₄, we cannot predict future levels of CH₄ and, by extension, predictions of stratospheric O₃ are rendered uncertain.

Table 3-13. Calculated Methane Flux — Shark River Slough Study Area

Habitat Category	Area	Flux/Ha/Day**	Total Flux/day
Sawgrass < 3.0 m	76,024 ha	870 g/ha/day	66.1 × 10 ⁶ g/day
Sawgrass/Spikerush	17,747 ha	400 g/ha/day	7.1 × 10 ⁶ g/day
Sawgrass/Cypress	18,688 ha	130 g/ha/day	2.4 × 10 ⁶ g/day
Swamp Forest	5,151 ha	720 g/ha/day	3.7 × 10 ⁶ g/day
Unsampled/ Negligible Flux	20,588 ha	—	—

*Area of individual habitats derived from a Landsat thematic mapper image obtained on 12/20/82.

**Flux estimates are derived from a large number of individual measurements made at different times and sites.

Unravelling the mysteries of the global CH_4 cycle will be very difficult. The present rise of CH_4 levels represents the net effect of changes (up or down) in tropospheric OH, which controls the sink for CH_4 , changes in wetland emissions due to land modification (reduced areas) and to climatic warming in the Arctic (increased source?), and changes in agricultural emissions from rice fields, cattle, and manure operations (increased source).

NASA recently initiated an interdisciplinary program to pursue this important problem. Determination of CH_4 atmospheric trends at various latitudes is one important step in this direction. The study of carbon and hydrogen isotopes in methane is a promising new area being actively explored. Recent work by Stevens and Engelkemeir (1985) illustrate the basic ideas being pursued. Figure 3-15 shows isotopic compositions for ^{13}C and ^{12}C in CH_4 (Stevens and Engelkemeir, 1985). Biogenic sources are generally depleted in ^{13}C relative to atmospheric CH_4 , while combustion and fossil fuel sources are isotopically heavier than atmospheric. One conclusion drawn from Figure 3-15 is that either non-biogenic sources must be unexpectedly important, or that presently unexplored biological sources must release relatively heavy CH_4 (Stevens and Engelkemeir, 1985). The data suggest that much insight could be obtained from detailed analysis of $^{13}\text{C}/^{12}\text{C}$ ratios of various sources combined with latitudinal, seasonal, and long-term trend data on the $^{13}\text{C}/^{12}\text{C}$ ratio in atmospheric CH_4 . Attention to detail is needed for this task since there could be seasonal or other variations of the $^{13}\text{C}/^{12}\text{C}$ ratio for major sources.

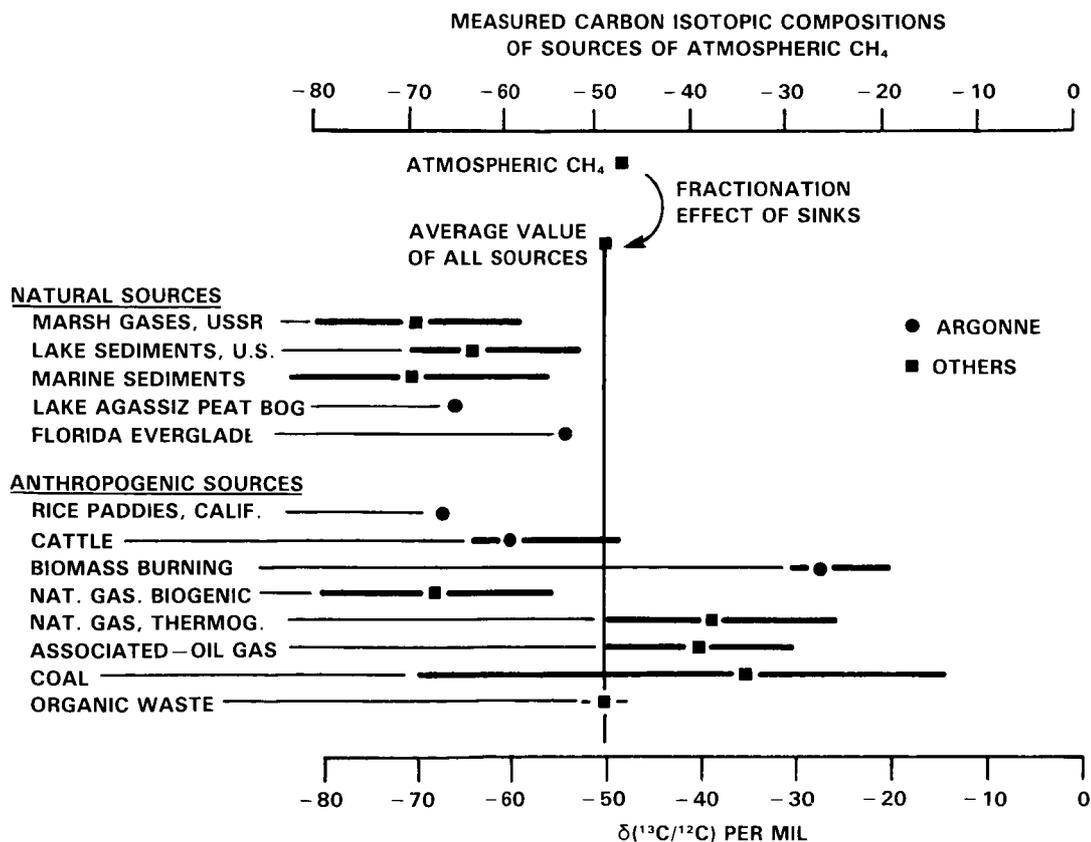


Figure 3-15. Summary of $^{13}\text{C}/^{12}\text{C}$ isotopic composition of major sources of atmospheric methane (Stevens and Engelkemeir, 1985).

SOURCE GASES

While the carbon isotopes offer promise for source analysis, the D/H ratio in CH₄ may provide useful diagnostics for the sink, since the OH reaction rate is much slower for CH₃D than for CH₄. Thus analysis of latitudinal and seasonal variations of CH₃D in the atmosphere, together with source characterization, may help to define atmospheric distributions of OH.

While CH₄ (1.6 ppm) dominates among global atmospheric hydrocarbons, tropospheric photochemistry and OH-O₃-CO global distributions are also strongly influenced by other, more reactive hydrocarbons, particularly isoprenes, terpenes, and the C₂-C₅ alkenes. While the global fields of these non-methane hydrocarbons have not yet been well characterized, some recent, representative measurements are given in Table 3-14.

3.5 CARBON MONOXIDE (CO)

The influence of CO on stratospheric chemistry, while indirect, may be extremely important. Increasing levels of CO tend to suppress levels of atmospheric OH, leading to longer lifetimes and higher concentrations of CH₄, CH₃CCl₃, and other species whose sinks are controlled by OH. Hence, factors controlling the atmospheric level of CO are vitally important to stratospheric chemistry as well as to tropospheric chemistry.

3.5.1 Distributions and Trends

Figure 3-16 presents a reconstruction of the global CO distribution from available data through 1980. There is an evident north-south gradient, with more CO in the north. There is significant excess for CO in the lowest layers of the atmosphere in the Northern Hemisphere, while in the south the vertical gradient is very small, with perhaps a slight excess aloft.

More recent measurements have focused on better determination of the vertical gradients (Seiler and Fishman, 1981; Newell *et al.*, 1981), on definition of the seasonal cycles at various latitudes (Khalil and Rasmussen, 1984b,c; Seiler *et al.*, 1984a; GMCC, 1982), and on satellite observations to delineate major source regions (Reichle *et al.*, 1985).

The seasonal variation of CO has been measured at several locations and is shown here (Figure 3-17) for Cape Point, South Africa (Seiler *et al.*, 1984b). Highest concentrations are observed during winter and lowest levels are observed in the summer at ground level in non-urban locations. The amplitude of the seasonal cycle varies with latitude, being greatest at higher latitudes and smallest at the equator (GMCC, 1982; Seiler *et al.*, 1984b; Khalil and Rasmussen, 1984b.c). At northern mid-latitudes, the seasonal cycle amounts to $\pm 25\%$ of the mean. These observations are in general agreement with the expected pattern, i.e. the inverse of the spatial and temporal variability of OH radicals which remove much of the CO from the atmosphere. Definition of the seasonal behavior has essentially resolved apparent inconsistencies among various data sets obtained at different times of year.

Satellite and aircraft data on mid-tropospheric CO clearly show expected enhancements due to industrial source regions in North America, Europe and Asia, as illustrated in Figure 3-16 to 3-18 (Fishman *et al.*, 1980; Reichle *et al.*, 1985). Important elevated regions were also found in the tropics, possibly associated with agricultural burning. Preliminary analysis of the tropical sources indicated a potentially large contribution to the global CO budget (Delaney *et al.*, 1984; Reichle *et al.*, 1984).

SOURCE GASES

Table 3-14. Recent Measurements of Light Hydrocarbons

COMPOUND	DATE	CONC \pm SD ppbv	LAT	REF	
C ₂ H ₆	1/81	8.00 \pm 1.60	40°N	1	
	6/80	2.97 \pm 2.67	40°S	3	
	1982	1.67	26°S	2	
	12/18,1/79	2.37, 2.1	35°N	2,5	
	12/81	1.86, 2.0	25°N	2,5	
	12/81	0.64, 2.0	10°N	2,5	
	12/81	0.28, 2.0	10°S	2,5	
	12/81	0.23, 0.75	25°S	2	
	12/81	27.56	0-20°N	3	
	6/82	0.85	13-30°N	4	
	11/82	0.40	0-40°S	4	
	C ₃ H ₈	1/81	8.50 \pm 1.60	40°N	1
		6/80	0.42 \pm 1.23	40°S	3
1982		0.42	26°S	2	
12/81,1/79		0.80, .85	35°N	2,5	
12/81		0.72, .90	25°N	2,5	
12/81		0.33, .50	10°N	2,5	
12/81		0.26, .20	10°S	2,5	
12/81		0.11	25°S	2	
12/82		10.86	0-20°N	3	
6/82		2.25	13-30°N	4	
11/82		0.10	0-40°S	4	
C ₄ H ₁₀		1/81	3.00 \pm 1.80	40°N	1
		6/80	0.34 \pm 0.33	40°S	3
	1982	0.59	26°S	2	
	12/81	0.51	35°N	2	
	12/81	0.60	25°N	2	
	12/81	0.48	10°N	2	
	12/81	0.16	10°S	2	
	12/81	0.14	25°S	2	
	12/81	9.22	0-20°N	3	
	11/82	0.05	0-40°S	4	
	C ₅ H ₁₂	1/81	3.00 \pm 2.40	40°N	1
		6/80	0.43 \pm 0.42	40°S	3
		1982	0.27	26°S	2
12/81		0.42	35°N	2	
12/81		0.43	25°N	2	
12/81		0.32	10°N	2	
12/81		0.33	10°S	2	
12/81		0.17		2	
12/81		0.99	0-20°N	3	
11/82		1.10	0-40°S	4	

SOURCE GASES

Table 3-14. Recent Measurements of Light Hydrocarbons — Continued

COMPOUND	DATE	CONC ± SD ppbv	LAT	REF
C ₂ H ₂	12/81,1/79	0.46, 0.45	35°N	2,5
	12/81	0.42, 0.40	25°N	2,5
	12/81	0.23, 0.30	10°N	2,5
	12/81	0.25, 0.10	10°S	2,5
	12/81	0.13,	25°S	2,
	2/82	7.62	0-20°N	3
C ₂ H ₄	6/80	2.70 ± 2.43	40°S	3
	1982	0.09	26°S	2
	12/81	0.12	35°N	2
	12/81	0.10	25°N	2
	12/81	0.08	10°N	2
	12/81	0.07	10°S	2
	12/81	0.08	25°S	2
	12/81	6.86	0-20°N	3
	6/82	2.10	13-30°N	4
11/82	0.20	0-40°N	4	
C ₃ H ₆	1/81	1.00 ± 1.10	40°N	1
	12/81,1/79	0.05, .25	35°N	2,5
	12/81,1/79	0.18, .25	25°N	2,5
	12/81,1/79	0.23, .25	10°N	2,5
	12/81,1/79	0.22, .20	10°S	2,5
	12/81	0.07	25°S	2
	12/82	3.30	0-20°N	3
	12/82	0.20	0-40°N	4
C ₅ H ₈		2.27 ± 2.23	40°S	3
C ₇ H ₈	1/81	3.00 ± 1.80	40°N	1
	6/80	0.14 ± 0.13	40°S	3
	12/82	5.24	0-20°N	3
C ₈ H ₁₀	1/81	3.00 ± 1.50	40°N	1
	6/80	0.14	40°S	3
	12/82	2.95	0-20°N	3

1. Sexton and Westberg, 1984.
2. Singh and Salas, 1982.
3. Greenberg and Zimmerman, 1984.
4. Bonsang and Lambert, 1985.
5. Rudolph and Ehhalt, 1981.

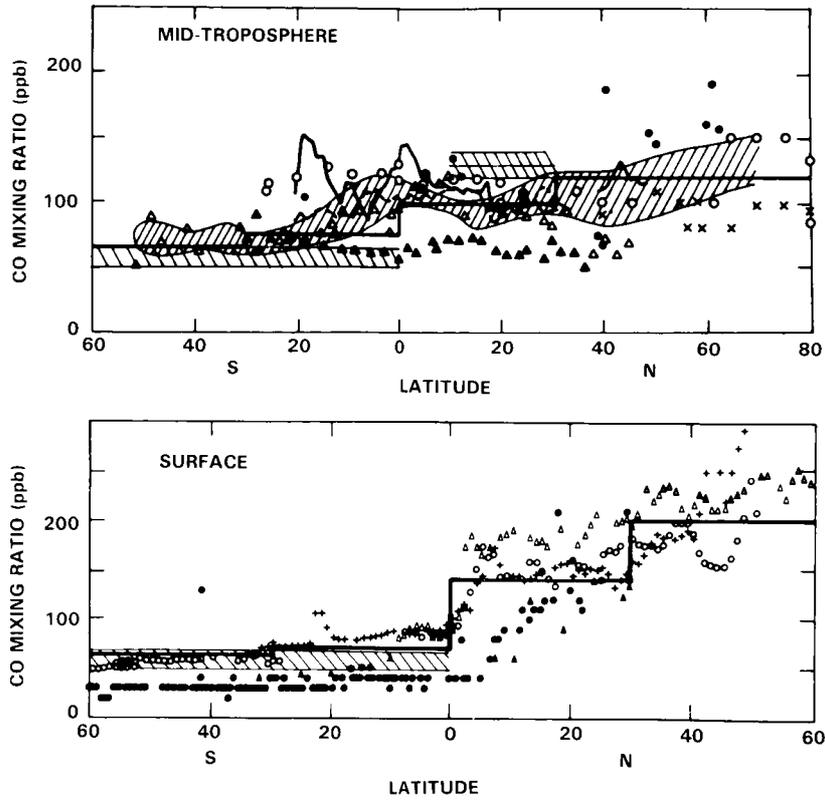


Figure 3-16. Summary of atmospheric CO measurements as a function of latitude for (a) mid-troposphere and (b) surface for the period 1967-78 (from Logan *et al.*, 1981). The heavy lines show average values for latitude zones 0, 30° (N,S) and 30, 90° (N,S).

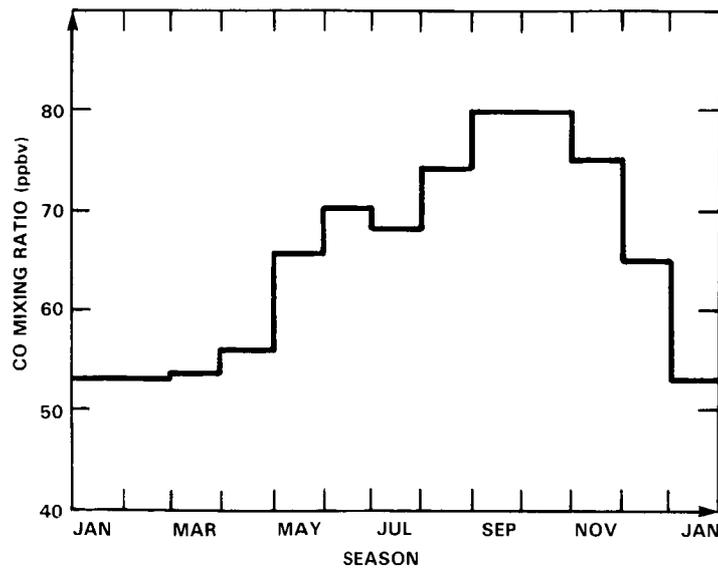


Figure 3-17. Seasonal variation of atmospheric CO mixing ratio (ppbv) measured at Cape Point, South Africa (34°S), 1978-81, (Seiler *et al.*, 1984b).

SOURCE GASES

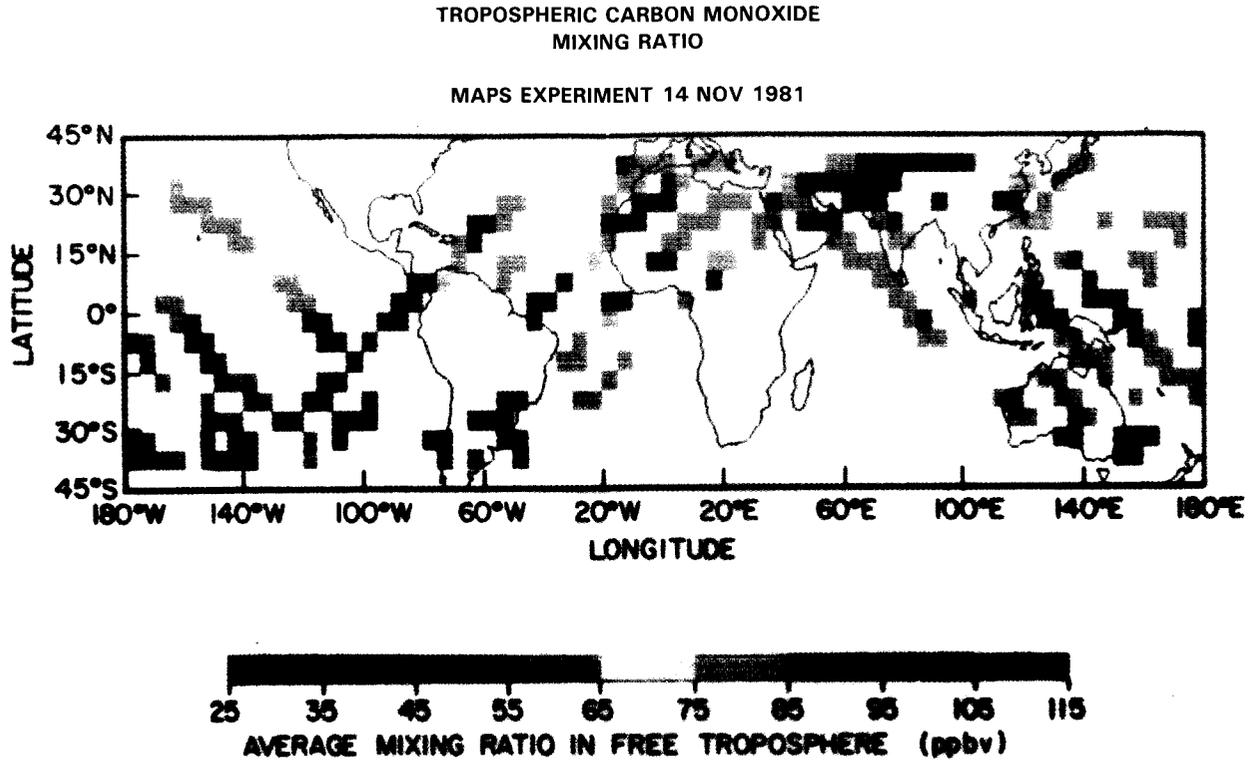


Figure 3-18. Average value of the volume mixing ratio of carbon monoxide in the free troposphere as measured by the Measurement of Air Pollution from Satellite (MAPS) experiment. The experiment was flown on $5^\circ \times 5^\circ$ squares, and they have a precision of a few percent (Reichle *et al.*, 1985).

Since large anthropogenic sources of CO have been identified, it is expected that concentrations of CO may be increasing on a global scale. Carbon monoxide is emitted from a large number of primarily land-based sources as well as from the atmospheric oxidation of CH_4 and other hydrocarbons. It reacts rather rapidly with OH radicals ($\bar{\tau} \approx 0.4$ yrs, $\tau_{\min} \approx 0.1$ yrs in the tropics). The short atmospheric lifetime allows concentrations of CO to vary considerably in both space and time, making it difficult to isolate slow increases representative of the long-term trend. Trends may be quite dependent on latitude. Nevertheless, some recent data have shown an increase in the concentration of CO that may represent a long-term trend, although the magnitude is still quite uncertain. One study (Khalil and Rasmussen, 1984b,c) indicated CO increases of about $5\% \text{ yr}^{-1}$ at Cape Meares, Oregon between 1979 and 1982. Subsequent measurements at this site lowered the estimated mean trend. Results presented by Dvoryashina *et al.* (1984) based on spectroscopic measurements of CO over the U.S.S.R. between 1971-1983, suggest a 1-2% increase during that period. Rinsland and Levine (1985) deduced values for CO over Switzerland in 1951 (from Migeotte's plates) and they estimated in mean annual increase of $\approx 2\% \text{ yr}^{-1}$ between 1951 and 1981 at that site.

Mean concentrations and variability are smaller for CO in the Southern Hemisphere than in the north. The dominant sources of CO in the south may be the oxidation of CH_4 and transport from the north. Comparison of recent measurements of CO at Cape Point, South Africa (1978-81) with shipboard data obtained in 1971-1972 indicates that CO in the Southern Hemisphere may have increased by $0.5\text{-}1\% \text{ yr}^{-1}$ (Seiler *et al.*, 1984b). Measurements of CO taken at Tasmania and the South Pole do not yet show statistically significant increases (Fraser *et al.*, 1984).

It appears from these rather sparse data that CO may be increasing on a global scale, with the most significant increases at mid-to-high northern latitudes. It is not yet possible to estimate accurately the rate of CO increase, which is statistically more difficult than for CH₄ or CO₂ due to the greater spatial and temporal variability of CO.

3.5.2. Sources

Table 3-15 presents a recent budget for CO, adapted from Logan *et al.* (1981). Estimates for combustion are derived from detailed emissions inventories which incorporate the results of many field measurements. (Readers are referred to reviews by Seiler and Crutzen (1980) and Logan (1983) for detailed discussion.) The ranges given in Table 3-15 amount to "only" about $\pm 50\%$, reflecting the considerable attention paid by environmental agencies to this subject. Since much of the uncertainty is associated with estimates of the quantity of fuel consumed (especially in the case of biomass burning), it appears that better definition of the CO cycle must attend development and deployment of CO monitoring instruments, on satellites and on the ground, on refinement of the global OH distributions, and on remote sensing of agricultural burning. Development of a complete picture of CO sources requires coordinated research sampling a variety of spatial and temporal scales, in a manner analogous to that discussed for CH₄.

3.5.3 Discussion

Anthropogenic activities account for about 40% of global CO emissions, and one would expect at least comparable increase in the global concentrations. High emissions of CO tend to suppress the concentration of OH (Wofsy, 1976), which can lead to positive feedback and more-than-proportionate increase in the CO abundance (Sze, 1977). However, it appears that elevated CO levels may be concentrated near the latitudes of maximum combustion sources, where NO_x may also be elevated due to combustion (cf. Fishman *et al.*, 1980). Coincident elevations of CO and NO_x may lead to enhanced photochemical activity, including significant ozone production (Crutzen, 1973; Chameides and Walker, 1973; Fishman *et al.*, 1979). Indeed, there is evidence of a correlation between high O₃ and high CO levels at northern midlatitudes indicative of enhanced photochemical activity (Fishman and Crutzen, 1978; Fishman *et al.*, 1980). It is possible that OH levels may actually be enhanced in the regions of high CO, due to excess NO_x, O₃, and other species. Thus, the possibility of OH-CO positive (or negative) feedback cannot be assessed without a good understanding of NO_x, O₃ and hydrocarbon distributions in the atmosphere.

It is important to note that present day concentrations of CO (and CH₄) are not in equilibrium with emissions, because CO and CH₄ are coupled, and the time constant for relaxation of the coupled OH-CO-CH₄ system may be several times longer than the 10 year lifetime of CH₄ (cf. Sze, 1977). This effect arises from the positive feedback discussed above: oxidation of CH₄ gives rise to an important source for CO, and CO and CH₄ are the dominant sinks for OH.

There is no direct evidence to define the time history for CO over past centuries, and hence one cannot accurately assess the extent of the CO rise due to anthropogenic activity. A number of factors suggest that increases probably are large, i.e. 2 or more times more CO today than in prehistoric times: the north/south gradient is of this order, present rates of increase appear to be substantial, and the source estimates break down to ~60/40 (natural/anthropogenic). If CO levels have indeed increased substantially over the globe, then atmospheric chemistry is very different today from the unperturbed state some centuries ago.

SOURCE GASES

Table 3-15. Carbon Monoxide^a (1984 concentrations 30–200 ppb)

A. <i>Atmospheric burden</i> (10^6 tons as C)	200
B. <i>Sinks + accumulation</i> (10^6 tons as C yr^{-1})	
reaction with OH	820 \pm 300
soil uptake	110
accumulation (5.5% yr^{-1})	10
total	940 \pm 330
C. <i>Sources</i> (10^6 tons as C yr^{-1})	
fossil fuel combustion	190
oxidation of anthropogenic hydrocarbons	40
wood used as fuel	20
oceans	20
oxidation of CH_4	260
forest wild fires (temperate zone)	10
agricultural burning (temperate zone)	10
oxidation of natural hydrocarbons (temperate zone)	100
burning of savanna and agricultural land (tropics)	100
forest clearing (tropics)	160
oxidation of natural hydrocarbons (tropics)	150
total	1060
D. <i>Tropical Contribution</i> (10^6 tons as C yr^{-1})	
burning	100
forest clearing	160
oxidation of hydrocarbons	150
total	410

^a From Logan *et al.* (1981), updated by Logan *et al.* (private communication, 1984).

3.6 CARBON DIOXIDE (CO_2)

Although carbon dioxide is not itself a photochemically active species in either the troposphere or the stratosphere, it must be included in any discussion of source gases because it is the single most important greenhouse gas in the atmosphere. Hence it will have a strong influence on the temperature-dependent photochemistry in the stratosphere. A second reason to include CO_2 is that it is the most abundant and best studied trace gas of the global carbon cycle. There are long, very precise and detailed time-series for atmospheric CO_2 at different latitudes (Figures 3-19, 3-20). Such records offer a critical history of the evolution of atmospheric-biospheric exchange, and will greatly facilitate the interpretation of the cycling of related trace gases of the carbon cycle (e.g. CH_4 , CO), whose secular increases have only very recently

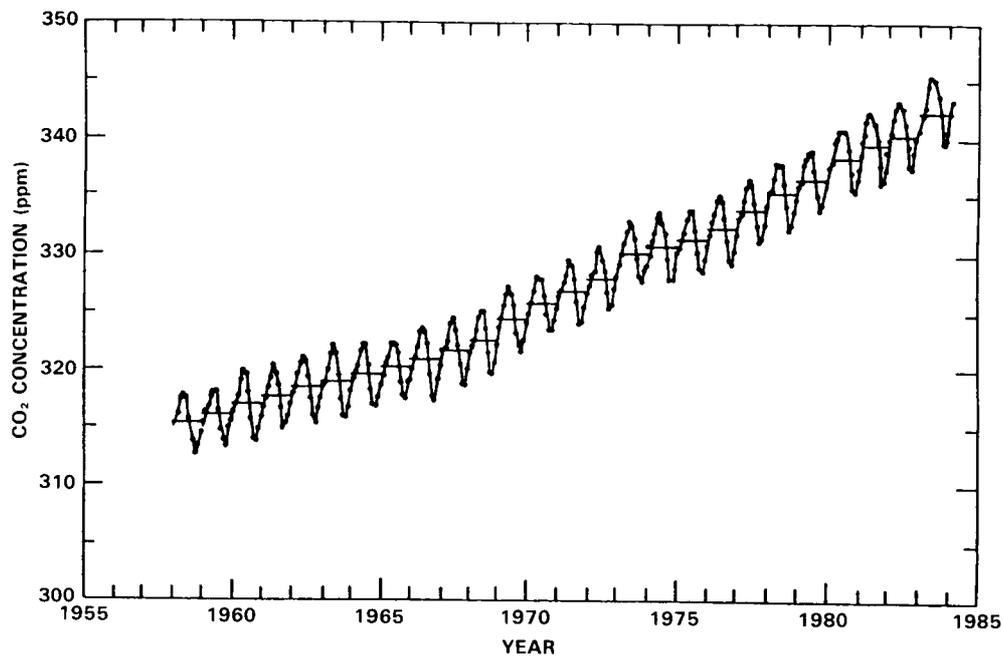


Figure 3-19. Concentration of atmospheric CO₂ at Mauna Loa Observatory, Hawaii, expressed as a mole fraction in ppm of dry air. The dots depict monthly averages of visually selected data which have been adjusted to the center of each month. The horizontal bars represent annual averages. Data obtained by C.D. Keeling, Scripps Institution of Oceanography, University of California, La Jolla, California, and are from files in the Carbon Dioxide Information Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

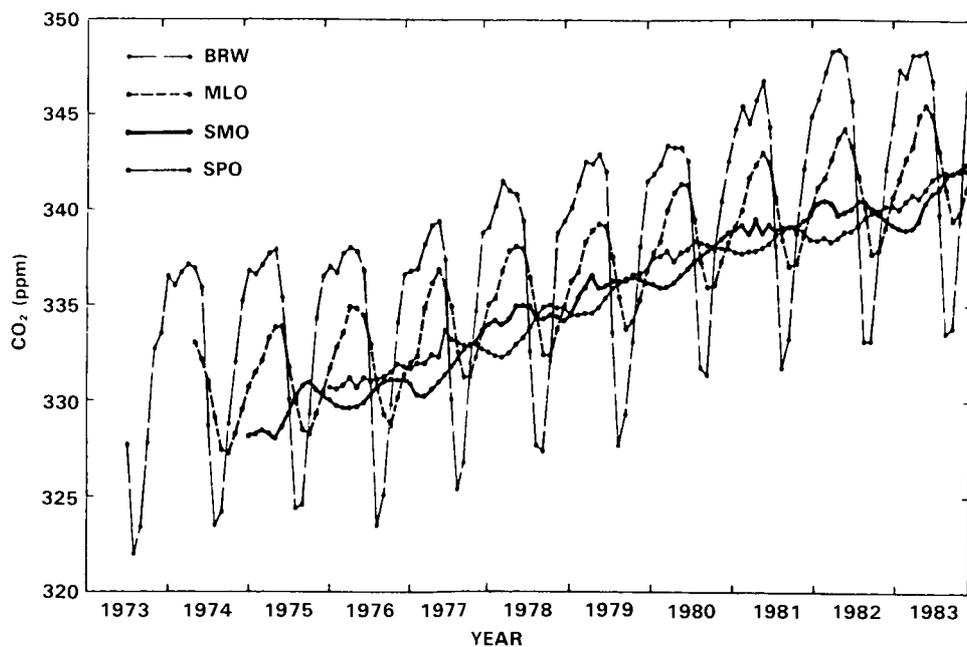


Figure 3-20. Provisionally selected monthly mean CO₂ concentrations from continuous measurements at the NOAA/GMCC baseline observatories (:Barrow, Alaska (BRW); Mauna Loa, Hawaii (MLO); American Samoa (SMO); South Pole (SPO). Values are in the WMO X81 mole fraction scale (Harries and Nicker-son, 1984).

SOURCE GASES

been established, and for which the mechanisms of change are much less well understood. Unlike the industrial sources of fluorocarbon gases, the biogenic sources of several important species (CO_2 , CH_4 , CO , N_2O , OCS , etc.) will likely *respond to*, as well as promote, climatic change. The inferences drawn from CO_2 studies on the working of the natural and perturbed carbon cycle will be essential for making accurate predictions of the evolving biogeochemical cycles of carbon, nitrogen, and sulfur under direct and indirect (climatic) human impact.

3.6.1 CO_2 Trends and Global Distribution

The modern period of direct, precise measurement of rising atmospheric CO_2 levels began with C.D. Keeling's time-series at Mauna Loa Hawaii (Figure 3-19, MLO) and at the South Pole during IGY (1958). Before this time, CO_2 measurements were of much lower quality, and of a less direct nature (see Gammon *et al.*, 1985a for a detailed review of the history of atmospheric CO_2 measurements and methods). Since the early 1970's, continuous measurements of CO_2 have been made by NOAA/GMCC at four remote stations: Barrow, Alaska; Mauna Loa, Hawaii; American Samoa, and the South Pole (Figure 3-20, Gammon *et al.*, 1985 a,b; Harries and Nickerson, 1984). The NOAA time-series at MLO agrees very well with the corresponding Keeling record. Recent interpretations of the global CO_2 distributions have been presented by Keeling *et al.* (1984), Keeling (1983), Pearman *et al.* (1983), Fraser *et al.* (1984), Bacastow *et al.* (1985), Komhyr *et al.* (1985).

A more detailed representation of the spatial and temporal variability of CO_2 near the earth's surface became possible in 1979 with the establishment of a global network of 20 cooperating air sampling sites coordinated by GMCC/NOAA. The CO_2 results from this network through 1983 have been recently described by Komhyr *et al.* (1985); the global CO_2 concentration surface for 1980-83 is shown in Figure 3-21. The observed CO_2 seasonal amplitude is dominated by land plants and soils in the northern mid-latitudes. Figure 3-22 shows the latitude dependence of the CO_2 seasonal amplitude (Gammon *et al.*, 1985b), which is strongly enhanced at northern middle and high latitudes.

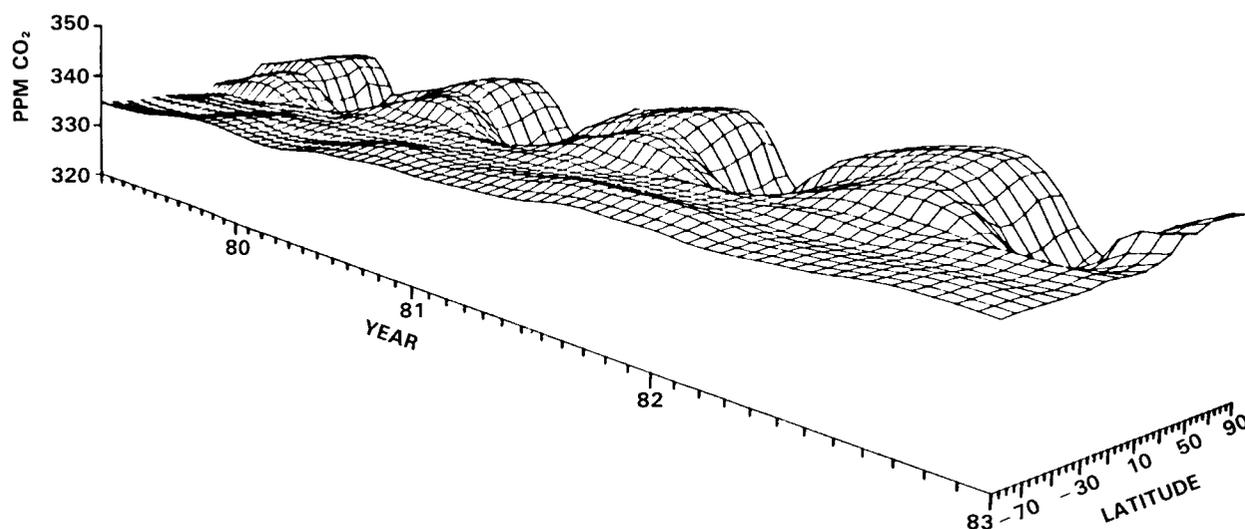


Figure 3-21. A three-dimensional perspective of the "pulse-of-the-planet," the variation of the global atmospheric CO_2 concentration in latitude and time based on flask measurements for 1979-1982. This zonally averaged surface has a resolution of 20 days and 10° in latitude and was synthesized from results of $\sim 10,000$ individual flask samples returned from 15 remote sea-level sites of the NOAA/GMCC sampling network (Komhyr *et al.*, 1985).

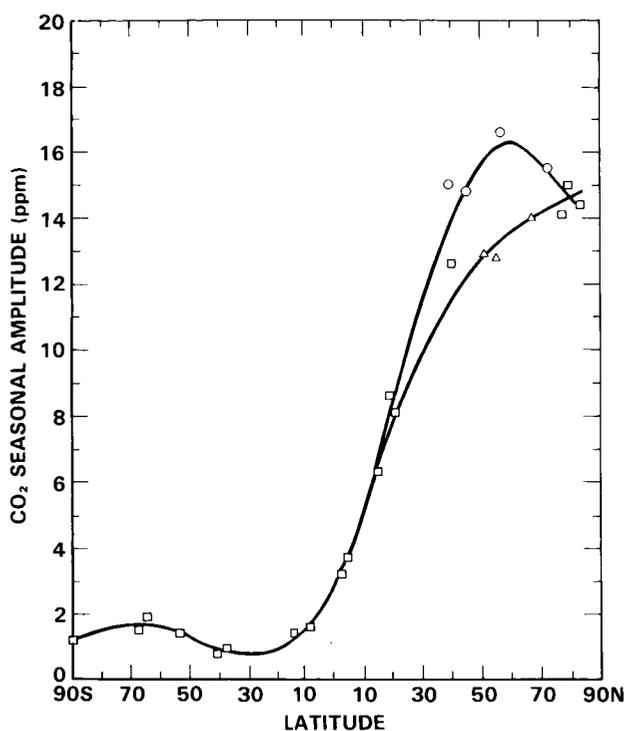


Figure 3-22. Latitude dependence of the atmospheric CO₂ seasonal amplitude as determined from surface stations (Komhyr *et al.*, 1985; Gammon *et al.*, 1985b). The separate curves at high northern latitude distinguished mid-ocean (Δ) from coastal (O) sites.

3.6.2 Discussion

Three examples are chosen below to illustrate: (1) the difficulty of establishing secular trends of biogenic trace gases in the presence of large interannual variability of natural origin; (2) the use of global trace gas data sets to interpret satellite remote sensing indices of global biospheric activity; and (3) the possibility that carbon cycle trace gas measurements offer a sensitive indicator of evolving atmosphere-biosphere exchanges in response to predicted climatic change. A summary of the temporal trends and variability observed for all three carbon cycle trace species (CO₂, CH₄, CO) is given in Table 3-16.

Natural Interannual Variability and El Nino:

The El Nino-Southern Oscillation perturbation of the global atmospheric CO₂ distribution is the strongest signal in the record after the local seasonal amplitude and long-term trends are removed. These CO₂ fluctuations are well correlated with both the Southern Oscillation Index and with regional sea surface temperature anomalies. The extraordinary 1982/83 ENSO event measurably perturbed the total global atmospheric burden of CO₂. The amplitude of the natural CO₂ fluctuation associated with an ENSO event is of order ± 0.5 ppm; for comparison, background air is currently ~ 345 ppm CO₂ in the global mean. Natural atmospheric CO₂ fluctuations of order 1 ppm (or 2 Gton carbon global atmospheric equivalent) correspond to small perturbations (1-2%) in the annual exchanges of the atmosphere-ocean (100 Gton C yr⁻¹) and atmosphere-biosphere (60 Gton C yr⁻¹) systems (Keeling, 1983). Fluctuations in the source-sink balance of either the biosphere or the ocean could be responsible for the observed atmospheric CO₂ fluctuations. Isotopic measurements (¹³CO₂) are useful in distinguishing between these two possibilities (Mook *et al.*, 1983).

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Table 3-16. Carbon Cycle Trace Gases: Summary of Measured Atmospheric Changes

Species	Tropospheric Concentration				Seasonality		Interannual Variability (in growth rate or seasonal amplitude)
	Present Level (1984, ppm) global mean	Secular Increase (% change in period) during decades			% Increase in Seasonal amplitude during decades		
		Past Century	1965-75	1975-85	1965-75	1975-85	
		% decade ⁻¹	% decade ⁻¹	% decade ⁻¹	% decade ⁻¹	% decade ⁻¹	
CO ₂	343.8 ± 0.2		3	4	≤ 2	10-20	Yes (ENSO)
CH ₄	1.67 ± .01		< 5	10-15	- ? -	- ? -	Yes (ENSO)
CO	~0.09 ± .02		- ? -	5-50	- ? -	- ? -	Yes?

The globally averaged year-to-year change in atmospheric CO₂ plotted by season (Figure 3-10c) clearly shows the effect of the 1982/83 ENSO event on the global atmospheric burden of CO₂ over at least a two-year period, from mid-1982 to mid-1984. The summer of 1982, relative to the fall of the previous year, showed no increase (0.0 ± 0.2 ppm yr⁻¹) in global CO₂ levels, implying that the equivalent of approximately 5×10^9 tons of fossil carbon burned during that interval was removed from the atmospheric reservoir for temporary storage in the near surface ocean, and (probably) in the land biosphere as well. Now, more than a year after the minimum in the Southern Oscillation Index (1/83), this missing 5 Gtons of carbon has been returned to the global atmosphere; the year-to-year CO₂ increase peaked in early 1984 at 2.2 ± 0.2 ppm yr⁻¹ before returning to the long-term mean growth rate of 1.4 ppm yr⁻¹ representative of the past decade. Since the past 5 years has been a period of nearly constant global combustion of fossil fuel ≈ 5 Gton yr⁻¹, the observed large interannual variations in atmospheric CO₂ are clearly *not* the result of changing rates of fossil fuel usage. One important conclusion is that secular trends extracted from time series measurements of biogenic trace gases are only reliable when the time span covers one or more major ENSO cycles (4-7 years), since large interannual variations in the growth rate have been observed for both CO₂ and CH₄. In the case of CO₂, these interannual variations have been shown to be correlated with interannual variation in tropospheric temperature in that latitude band (Gammon *et al.*, 1985b). In the case of CH₄, the oceanic content is only $\sim 1/300$ of the atmospheric burden, and the variations shown in Figure 3-10 must therefore arise from variations in terrestrial sources.

Atmospheric CO₂ and the Global Biosphere:

There is large uncertainty in assessing the global response of the land biosphere to the altered temperature and precipitation patterns which accompany a major El Nino event. While regional crop failures, floods and droughts are well documented, the globally integrated biospheric response and its effect on atmospheric CO₂ and other biogenic trace gases is harder to estimate. There is some recent evidence from satellite monitoring of the "vegetation index" of land plant activity that 1982 was a better growing season globally than 1983 (Fung *et al.*, 1985). This suggests that some fraction of the 5 Gtons of carbon missing from

the global atmosphere in the summer of 1982 may have been temporarily stored in the biosphere. Global surface measurements of seasonally varying CO₂ recently have been shown to relate directly to the seasonal photosynthetic activity of land plants as indicated by satellite indices of green-leaf matter (Tucker *et al.*, 1985; Fung *et al.*, 1985; Figure 3-23).

Increasing Amplitude of the CO₂ Seasonal Cycle: A Climate Signal?

The regular variation of atmospheric CO₂ levels by season and latitude in the Northern Hemisphere is dominated by the seasonal exchange between the atmosphere and the land biosphere and soil carbon reservoirs (Figures 3-21, 3-22). Any major change in either photosynthetic uptake or respiratory release of carbon will alter the observed CO₂ seasonality, which represents the local imbalance of these two opposing processes. While the first attempt to find such secular changes in the CO₂ seasonal amplitude at Mauna Loa (Hall *et al.*, 1975) were not successful, more recent investigations *have* found large and significant growth rates in the seasonal amplitude at several Northern Hemisphere locations (MLO, 'P', BRW), especially during the past decade (Pearman and Hyson, 1980; Cleaveland *et al.*, 1983; Bacastow *et al.*, 1985; Komyr *et al.*, 1984; Keeling *et al.*, 1984). At Mauna Loa, the mean rate of increase has been $\sim 0.7\% \text{ yr}^{-1}$ from 1958 to 1982, resulting in a 20% increase (5.5 \rightarrow 6.5 ppm) in the CO₂ seasonality over this interval (Bacastow *et al.*, 1984). For comparison, the corresponding percentage increase in CO₂ concentration has been only 9%. The amplitude increase before 1975 was slight ($\sim 0.2\% \text{ yr}^{-1}$). However, since 1975, the increase in amplitude has been very rapid ($\sim 2\% \text{ yr}^{-1}$ or $\sim 0.1 \text{ ppm yr}^{-1}$). Similar rates of increase in the local CO₂ seasonality, have been recently reported for the long CO₂ records at more northerly stations (Weathership 'P', Keeling *et al.*, 1984; Barrow, Alaska, Bacastow *et al.*, 1985). While the NOAA/GMCC flask and continuous records at MLO and BRW extend only over the last decade, they also exhibit CO₂ seasonality growth rates of 1-2% yr^{-1} over this period. The CO₂ amplitude changes at all northern latitudes have been similar in absolute terms (0.1-0.2 ppm yr^{-1}), the largest rates of increase ($\sim 0.2 \text{ ppm yr}^{-1}$) observed in the Arctic (BRW).

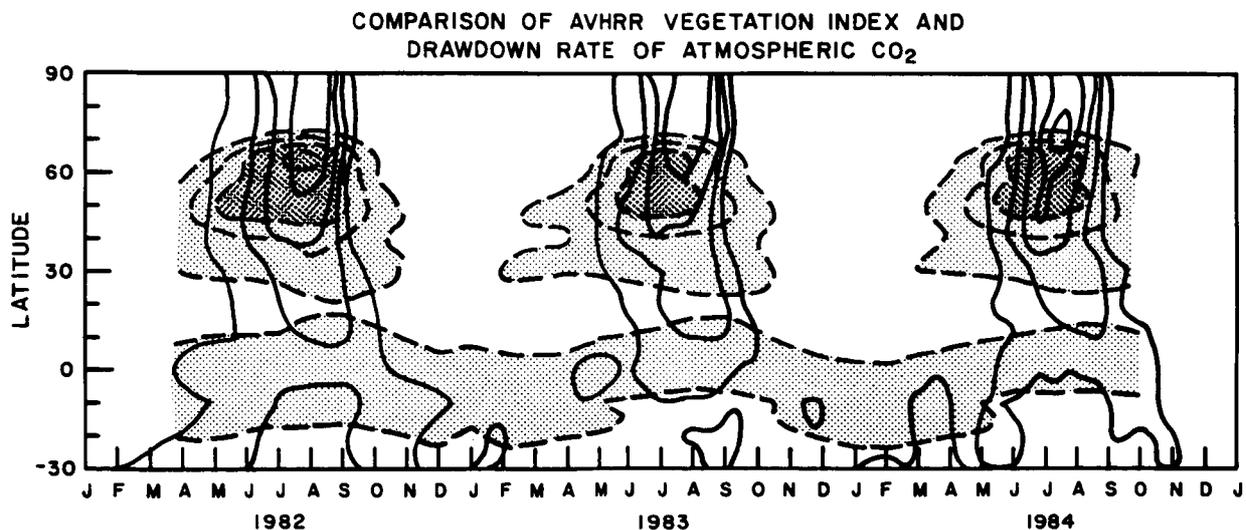


Figure 3-23. Overlay of the seasonal variation of atmospheric CO₂ with the seasonal variation of satellite-derived indices of photosynthetic activity of land plants ("normalized difference vegetation index") (Tucker *et al.*, 1986; Fung *et al.*, 1986). The dashed contours and the shaded regions represent the zonally averaged vegetation index; contour interval is 0.1. The solid contours represent negative values of $d\text{CO}_2/dt$, the rate of summer draw-down of atmospheric CO₂ by the land plants. Contour interval is -2 ppm/month . Positive values of $d\text{CO}_2/dt$ representing fall respiration are not reflected in corresponding variations of the vegetation index and are not plotted. Both CO₂ draw-down rates and vegetation indices peak at high (60° - 70°N) northern latitudes in July-August.

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As discussed by Keeling (1983) and Bacastow *et al.* (1985), an increasing CO₂ seasonal amplitude indicates 'increased plant activity,' but not necessarily increased net carbon storage. The observed percentage increase in northern hemisphere CO₂ seasonality is more than twice that of the CO₂ concentration, which suggests that any 'fertilization effect' (i.e. enhanced photosynthesis by the land biosphere in a higher CO₂ environment) could explain only a small fraction of the observed change in seasonal amplitude.

The seasonality of fossil fuel release is also insufficient to explain the increase (Pearman and Hyson, 1980). A more likely explanation is to be found in the strong temperature dependence of respiration of CO₂ from plants and soils and the observed warming trend over the last decade in the northern hemisphere. Harmonic analyses of the secular changes in CO₂ amplitude at each site may reveal whether enhanced photosynthesis (annual) or enhanced respiration (semi-annual) is more important. A first look at the NOAA/GMCC continuous CO₂ records since 1975 suggests that the changing seasonality of MLO is largely due to enhanced summer photosynthetic fixation of CO₂, while at BRW, spring and fall respiration pulses contribute equally to an enhanced summer draw down as causes of the CO₂ amplitude increase. If the amplitude increase is proportional to the local amplitude, then the largest absolute changes are predicted to occur in the latitude band 50-60°N where the CO₂ seasonal amplitude itself is maximum.

As noted above, the second most important trace gas of the carbon cycle, methane, is now known to be increasing in the atmosphere at ~1% yr⁻¹. There is evidence to suggest that the percentage rate of the CH₄ increase has become more rapid during the last decade (cf. Ehhalt *et al.*, 1983b). If the locus of the source region driving the atmospheric CH₄ increase is found to be the same as that for the CO₂ seasonal amplitude increase, then a strong argument can be made that both phenomena represent a response of the Northern Hemisphere biosphere and soil carbon pool to the incipient climate change predicted for the coming decades. Thus the change in CO₂ seasonality may be the first indication of a positive feedback loop involving atmospheric CO₂, boreal climate, and soil carbon reservoirs. Increasing levels of CH₄ may also reflect these interactions, at least in part.

Table 3-16 summarizes current knowledge of the temporal behavior of the major gases of the carbon cycle (CO₂, CH₄, CO) during the past century and in particular during the past two decades. Clearly, CO₂ has been most intensively studied and is best understood. However, the relative roles of the ocean versus the land biota in producing the El Nino-related variability is very uncertain, as is the cause for the sudden onset of an increase in the seasonal amplitude during the past decade. For CH₄, the seasonal amplitude is not yet well enough defined to detect secular amplitude changes, although the CH₄ concentration itself is observed to be increasing more rapidly since 1975 than in the previous decade. For CO, the observations are even more limited in space and time than for CH₄, although some growth in the atmospheric CO level during the past decade has been reported, perhaps more rapid in far northern latitudes (1-4% yr⁻¹) than in southern latitudes (0-0.5% yr⁻¹). Of the carbon-cycle gases, the perturbation of the atmospheric concentration from pre-industrial levels seems to have been greater for CH₄ than for CO₂. Preindustrial levels of CO are unknown. Levels and growth rates for N₂O are included for comparison to illustrate that the primary biogenic trace gases of both the carbon (CH₄, CO₂) and nitrogen (N₂O) cycles have experienced an acceleration in their rate of atmospheric increase during the past decade.

3.7 SOURCE GASES FOR STRATOSPHERIC SULFATE AEROSOLS (OCS, CS₂)

While most sulfur gases emitted into the troposphere from natural and anthropogenic sources are too reactive and/or too soluble to reach the stratosphere, OCS is an important exception (Crutzen, 1976; Sze and Ko, 1979). Apart from volcanic injection, the major source of sulfur to the stratosphere is OCS from

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the troposphere. Thus, as for CO₂, the major role of OCS in stratospheric chemistry is indirect, via the role of the stratospheric sulfate aerosol layer in influencing the temperature structure in the lower stratosphere (18-22 km).

Carbonyl sulfide (OCS), has an atmospheric lifetime greater than one year. The OCS concentration in the free troposphere (500 ppt) is many times greater than other sulfur gases (Torres *et al.*, 1980), and therefore is a major source of sulfur to the background (non-volcanically perturbed) stratospheric sulfate layer (Crutzen, 1976; Turco *et al.*, 1980). The present anthropogenic sources appear to be a relatively small fraction of the total global emissions (Khalil and Rasmussen, 1985b, Table 3-17). Johnson (1985)

Table 3-17. Global Sources and Sinks of Carbonyl Sulfide and Carbon Disulfide*

	OCS		CS ₂	
	Estimate	Range	Estimate	Range
Sources (Tg y⁻¹)				
Oceans	0.60	0.3 - 0.9	0.6	0.2 - 0.7
Soils	0.40	0.2 - 0.6	0.9	0.5 - 2
Volcanoes	0.02	0.01 - .05	0.02	< 0.1
Marshes	0.02	0.01 - 0.06	0.1	0.05 - 0.2
Biomass burning	0.20	0.1 - 0.5	—	—
Coal-fired power plants	0.08	0.4 - 0.15	—	—
Automobiles, chemical industry and sulfur recovery processes	0.06	0.01 - 0.3	0.37	< 0.7
Subtotal	1.4	≤ 3	2	≤ 4
CS₂ → OCS:				
CS-photochemistry and OH reactions	0.60	0 - 2	0	0
Total	2	≤ 5	2	≤ 4
Global burdens (Tg)	4.6	3.8 - 5	0.07	0.04 - 0.1
	(500 pptv)		(20 pptv)	
Lifetime (y)	2-2.5	≥ 1	13 days	>4 days
Sinks (Tg y⁻¹)				
OH reaction	0.8	0.1 - 1.5	0.6	≤ 4
Stratospheric photolysis	0.1	≤ 0.2	0	0
O atom reaction	0.03	—	0.1	< 0.2
Other	1.1	≤ 3.3	1.3	< 3

* The estimated emissions are consistent with observed distributions of OCS and CS₂ according to a global mass balance (see text). All combinations of emissions within the ranges given above may not be consistent.

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has reviewed remote tropospheric measurements of OCS over a seven year period by four different groups and estimated that the maximum secular trend was $\pm 3\%$ per year and the most likely value was much closer to zero (Table 3-18). Torres *et al.* (1980) found the north-to-south interhemispheric gradient to be less than 10% from aircraft measurements in the free troposphere; from shipboard measurements in the marine boundary layer, Johnson (1985) set a limit on the meridional gradient within the Northern Hemisphere of less than 7%. Less is known about longitudinal gradients, expected to be smaller than latitudinal gradients except near strong regional sources.

Carbon disulfide (CS_2) has an atmospheric lifetime of a few weeks, giving it an extremely low upper tropospheric concentration (6 ppt at 6 km, Tucker *et al.*, 1985), so that it does not directly affect the stratosphere. However, it appears that the atmospheric oxidation of CS_2 by OH produces OCS, so that atmospheric CS_2 is likely a major source of tropospheric OCS (Sze and Ko, 1979; Jones *et al.*, 1983; Barnes *et al.*, 1983). Hence, the OCS distribution may be influenced by emissions of CS_2 from industrial sources. A detailed assessment is impossible at present due to the scant knowledge about actual source strengths for OCS or CS_2 from natural and anthropogenic sources.

3.8 VOLCANIC INJECTIONS OF CHLORINE INTO THE STRATOSPHERE

Volcanoes have long been recognized as dominant sources of stratospheric sulfate and aerosol. It has also been clear for some time that volcanoes could be sources of stratospheric chlorine (Stolarski and Cicerone, 1974). Very little research has been done to quantify this source. Only a fraction of volcanic eruptions penetrate the stratosphere: The amount of volatile material in the pre-eruption magma varies from volcano to volcano, the amount of chlorine in the volatile material varies similarly, and soluble, polar compounds like HCl can be removed during the rapid rise (and condensation) of a volcanic plume. Hence volcanoes are sporadic sources not easily described by annual averages.

Two recent studies contribute new information. Johnston (1980) measured the amounts of chlorine in ashfall from the 1976 Augustine (Alaska) eruption and compared these amounts to those found in pre-eruption magmas. Johnston concluded that this volcano might have injected $(82 \text{ to } 175) \times 10^9$ g of HCl into the stratosphere and that the potential injections of volcanoes have been underestimated in general.

Table 3-18. A History of Atmospheric OCS Measurements. All Measurements Were Made in the Spring of the Indicated Year Except for the First Set Which Was Made in the *Fall* of 1975. The OCS Concentration is Given in Units of ppt.

Investigator(s)	Location	Date	OCS
Sandalls and Penkett	England	1975	510
Maroulis <i>et al.</i>	USA	1977	467
Torres <i>et al.</i>	Pacific Ocean, 70°N-57°S	1978	512
Hoyt	Pacific Ocean, 46°N-12°N	1981	505
Johnson, 1985	Pacific Ocean, 53°N-16°N	1982	502
	Pacific Ocean, 50°N-6°S	1983	517

Following the 1982 El Chichon (Mexico) eruption, Mankin and Coffey (1984) detected an increase of about 40% in the stratospheric column of HCl between 20° and 40°N. Their measurements were by infrared absorption from aircraft, thus, their results are specific to HCl. Lacking observations below 18°N and above 41°N, they could only assume the spatial distribution of the HCl increase elsewhere. They estimated that the volcano injected about 4×10^{10} g HCl into the stratosphere. Based on their previous observations in northern midlatitudes, Mankin and Coffey have provided solid evidence of input from El Chichon but even so we do not know the initial form of the chlorine (Cl₂ or HCl), its altitude distribution and whether gas-particle interactions extended strong control over the partitioning of gaseous and aerosol chlorine.

3.9 SECULAR TRENDS OF TRACE GASES FROM POLAR ICE CORES

A recently developed technique for trace gas analysis of air bubbles trapped in polar ice now offers the promise of detailed atmospheric histories for climate-linked trace gases dating back hundreds to thousands of years ago. Thus the composition of the atmosphere may be inferred for times long before human activity had begun to alter it. So far concentrations of CO₂, CH₄, CCl₃F and CCl₂F₂ have been measured in the bubbles of ice cores (Delmas *et al.*, 1980; Berner *et al.*, 1980; Neftel *et al.*, 1982, 1985; Stauffer *et al.*, 1985; Oeschger, 1985; Robbins *et al.*, 1973; Khalil and Rasmussen, 1982; Craig and Chou, 1982; Rasmussen and Khalil, 1984b), and preliminary data have appeared for N₂O (Pearman, *et al.* 1985).

The preindustrial levels of CO₂ have been determined to be between 260 and 280 ppmv (Delmas *et al.*, 1980; Neftel *et al.*, 1982, 1985; Zumbunn *et al.*, 1982; Raynaud and Barnola, 1985; Pearman *et al.*, 1985). Measurements of methane show that atmospheric concentrations before about 150-200 years ago were less than half of the present concentrations (Robbins *et al.*, 1973; Khalil and Rasmussen, 1982; Craig and Chou, 1982; Rasmussen and Khalil, 1984b).

The concentrations of CFC₁₃ and CF₂Cl₂ were found to be below the detection limits of around 10 pptv in the ice cores, confirming that the present concentrations are due entirely to recent industrial emissions (Khalil and Rasmussen, 1982; Rasmussen and Khalil, 1984b).

It is expected that the concentrations of a large number of other trace gases, including N₂O, CO, OCS and non-methane hydrocarbons may be obtained from the polar ice cores as better methods are developed for extracting the air without melting the ice. These measurements can provide unique information on the undisturbed natural state of the atmosphere. Recently reported measurements of ¹³C/¹²C in CO₂ from Antarctic ice (Friedli *et al.*, 1984) suggest that isotopic time series for trace gases in ice cores may soon provide detailed information on the evolution of particular sources in recent centuries.

3.10 SUMMARY AND RESEARCH RECOMMENDATIONS

Overview of atmospheric trends

Halocarbons, methane, nitrous oxide, odd nitrogen, and carbon monoxide are the most important, globally distributed trace gases in the atmosphere, exerting powerful direct and indirect influence on stratospheric chemistry. Concentrations of all of these gases appear to be increasing at present on a global basis, by 5% yr⁻¹ for CFC-11 and CFC-12, 7% yr⁻¹ for CH₃CCl₃, 1% yr⁻¹ for CH₄, 0.2% yr⁻¹ for N₂O, and 1-2% yr⁻¹ for CO. Available evidence indicates that increases in levels of CH₄, CO₂ and N₂O have been sustained for long periods and the increases derive from nondiscretionary, large scale human activities, mainly food and energy production. From this viewpoint, it would be expected that trends in CO and

SOURCE GASES

NO_x may also have been sustained for a long time. It seems improbable, therefore, that present trends toward increasing concentrations will be arrested or reversed in the near future. On the contrary, analysis of the historical record and the present imbalances between sources and sinks suggest that we might anticipate a gradual acceleration of present increases, and that substantial rates of accumulation in the atmosphere should be sustainable for long periods. This view is conditioned on the postulate that global population and associated economic activity will continue to increase at appreciable rates for some time. We reach similar conclusions in the case of halocarbons which are purely of industrial origin.

Research recommendations-tropospheric gases

The discussion in this chapter focusses attention on a number of important research needs.

1. Continued development of baseline measurements for CH_4 , N_2O , halocarbons and other species will play a major role in resolving questions raised here. Improved temporal and spatial resolution of the monitoring networks will require close cooperation between individuals, agencies and various national programs active in this field. Important information can be obtained by high frequency observations at sites near source regions (e.g. Adrigole).

2. It is important to undertake flux measurements of biogenic gases from representative ecosystems, especially for CO_2 , CH_4 , N_2O and NO , in order to understand past and future trends in the composition of the atmosphere. Studies of the underlying biological and geochemical processes are essential components of this effort, since we must understand the factors regulating observed fluxes.

3. The fate of NO_x from biomass burning and from industrial sources needs to be studied since addition of NO or NO_2 to the middle troposphere can have a major influence on global OH levels. Much better definition of the NO_x distribution in the atmosphere is a prerequisite for this analysis. Studies of stratosphere-troposphere exchange are also needed.

4. Definition of trends and distributions for tropospheric CO is essential. A satellite-borne CO sensor, operating for extended periods (\sim years), could help enormously. This appears to be technically feasible. Expanded measurements of CO at baseline network stations should provide valuable data also.

5. Improved analytical precision, to ± 1 ppb, is needed in both synoptic and baseline studies of N_2O . Research on N_2O sources would benefit greatly from this instrumentation, which appears to be technically feasible using diode laser technology.

6. Methane isotopic studies promise to help define the relative contributions made by various sources.

7. Studies of trace gases in ice cores help enormously by putting present perturbed atmospheric gas concentrations in the context of the pre-industrial (i.e. natural) atmosphere, and by localizing the epoch when particular species began to increase.

8. Strong efforts should be made to obtain better release data for industrial halocarbons from all major producers, including the USSR, China and Eastern Europe.

Some of the above elements have been incorporated in the proposed Global Tropospheric Chemistry Program (NAS, 1984), and in components of NASA, NSF, and NOAA research programs. It should be clear from the discussion above that a high priority should be attached to these efforts in order to improve understanding of factors which influence stratospheric chemistry.