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CHAPTER 1

Source Gases: Concentrations, Emissions, and Trends

Authors:

P. Fraser
S. Penkett
R. Harriss
Y. Makide
E. Sanhueza

Additional Contributors:

F. Alyea
D. Blake
D. Cunnold
J. Elkins
M. Hirota
R. Prinn
R. Rasmussen
S. Rowland
T. Sasaki
H. Scheel
W. Seiler
P. Simmonds
P. Steele
R. Weiss

Chapter 1

Source Gases: Concentrations, Emissions, and Trends

Contents

SCIENTIFIC SUMMARY 1.1

1.1 INTRODUCTION 1.3

1.2 CFCs AND CARBON TETRACHLORIDE: GLOBAL DISTRIBUTIONS, TRENDS AND CALIBRATION 1.3

1.2.1 CFC-11 and CFC-12 ..... 1.3
1.2.2 CFC-113 ..... 1.7
1.2.3 CFC-114 and CFC-114a 1.8
1.2.4 Carbon Tetrachloride 1.8

1.3 METHYL CHLOROFORM AND HCFC-22 ..... 1.11

1.3.1 Global Distributions and Trends 1.11
1.3.2 Methylchloroform Calibration 1.14
1.3.3 Methylchloroform Lifetime and the Global OH Abundance 1.14
1.3.4 HCFC-22 Lifetime 1.15

1.4 OTHER CHLORINATED SPECIES 1.15

1.4.1 Methyl Chloride 1.15
1.4.2 Chloroform 1.15

1.5 HALONS AND OTHER BROMINATED SPECIES 1.15

1.6 CARBONYL SULPHIDE 1.16

1.7 NITROUS OXIDE 1.16

1.7.1 Atmospheric Distributions and Trends 1.16
1.7.2 Global Nitrous Oxide Budgets 1.18

1.8 METHANE 1.19

1.8.1 Atmospheric Distributions and Trends 1.19
1.8.2 Methane Sinks 1.23
1.8.3 Methane Sources 1.23
1.8.4 Global Methane Budgets 1.24

Contents (Continued))

1.9 HYDROGEN 1.25

1.9.1 Global Distribution and Trends 1.25
1.9.2 Sources and Sinks 1.25

1.10 CARBON MONOXIDE 1.25

1.10.1 Atmospheric Distributions and Trends 1.25
1.10.2 Carbon Monoxide Calibration 1.26
1.10.3 Global Carbon Monoxide Budgets 1.29

1.11 NON-METHANE HYDROCARBONS (NMHCs) 1.30

1.11.1 Sources and Sinks for NMHCs 1.30

1.12 CARBON DIOXIDE 1.31

1.12.1 Atmospheric Distributions and Trends 1.31
1.12.2 Sources and Sinks of CO_2 ..... 1.31

REFERENCES 1.31

SCIENTIFIC SUMMARY

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

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

CFC-11 and CFC-12 trends have not changed significantly since the last assessment. The global CFC-113 trend in 1989 (≈5–6 parts per trillion by volume (pptv), 9 percent) is higher than observed in 1987 (≈4–5 pptv, 7 percent). Absolute calibration remains uncertain (±10 percent). The global average CCl_4 concentration for 1989 (≈107 pptv) is lower than that reported for 1987 in the last assessment (≈140 pptv), due essentially to a change in calibration based on a comparison of Atmospheric Lifetime Experiment–Global Atmospheric Gases Experiment (ALE–GAGE) data with data collected in several other programs. Absolute calibration remains uncertain (±10 percent).

The CH_3CCl_3 global trend in 1989 from the ALE–GAGE program (5.5 pptv, 3.7 percent) is lower than that reported for 1987 (6.0 pptv, 4.0 percent). Absolute calibration remains uncertain (±10 percent), and the ALE–GAGE calibration could be high by ≈15 percent, inferring a global mean 1989 concentration of 135 pptv rather than 150 pptv based on the current ALE–GAGE calibration scale. The oceans are a significant sink for CH_3CCl_3, implying that computed OH levels are 5–10 percent too high if this sink is ignored. These variations are well within the uncertainty of the rate of methyl chloroform-hydroxyl radical reaction (±40 percent). By analogy, HCFCs and HFCs may also have an oceanic sink although HCFCs and HFCs are more resistant to hydrolysis than CH_3CCl_3. Assuming that the ALE–GAGE calibration and industrial emissions are accurate, then the CH_3CCl_3 trend implies that the CH_3CCl_3 sink and hence global OH levels are increasing by 1.0±0.8 percent per year.

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

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

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

The rate of increase of global tropospheric CH_4 continues to decline, with increases of 17–21 ppbv per year observed during 1978–1982 and 12–14 ppbv per year during 1988–1990, or even lower in the Southern Hemisphere. No satisfactory explanation of this phenomenon has been put forward. Ice core studies indicate that CH_4 growth rates have shown significant temporal variability over the past 100 years. The problem of reconciling atmospheric CH_4 observations with estimates of emission sources is severely limited by the lack of

observations in major source regions. There is significant uncertainty in the direct estimates of CH_4 emissions from rice agriculture. Indian studies suggest that the global CH_4 source from rice agriculture may be significantly lower than 100 Tg per year. Recent methane isotopic studies suggest that approximately 20 percent of the total methane source (500 Tg [10^{12} g] per year) is fossil, and 10 percent is from biomass burning. The CH_4 sink due to OH oxidation may be increasing due to increasing levels of OH radical. Global levels of H_2 are increasing (0.5–0.7 percent per year), presumably partly in response to growing CH_4 levels.

Increasing CO concentrations of about 1 ppbv per year appear to be confined to the Northern Hemisphere. In the Southern Hemisphere there have been periods of CO growth (1986–1988) and decline (1983–1985), with no overall change from 1978 to 1990. Some CO sources are known to be increasing (CH_4) and others decreasing (fuel CO emissions from OECD* countries). The CO sink due to OH oxidation may also be increasing due to increasing levels of OH radical.

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

1.1 INTRODUCTION

Source gases are defined as those gases that influence levels of stratospheric ozone (O_3) by transporting species containing halogen, hydrogen, and nitrogen to the stratosphere that are important in O_3 destruction. Examples are the CFCs, methane (CH_4), and nitrous oxide (N_2O). Other source gases that also come under consideration in an atmospheric O_3 context are those that are involved in the O_3 or hydroxyl (OH) radical chemistry of the troposphere. Examples are CH_4, carbon monoxide (CO) and nonmethane hydrocarbons (NMHCs). Most of the source gases, along with carbon dioxide (CO_2) and water vapor (H_2O), are climatically significant and thus affect stratospheric O_3 levels by their influence on stratospheric temperatures. Carbonyl sulphide (COS) could affect stratospheric O_3 through maintenance of the stratospheric sulphate aerosol layer, which may be involved in heterogeneous chlorine-catalyzed O_3 destruction.

This chapter updates the previous reviews of trends and emissions of source gases, either from the context of their influence on atmospheric O_3 (WMO, 1986; 1990a, b) or global climate change (IPCC, 1990). The current (1989) global abundances and concentration trends of the trace gases are given in Table 1-1.

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

The CFCs (-11, -12, and -113) and carbon tetrachloride (CCl_4) compose 70 percent of the anthropogenic organochlorine loading of the troposphere (CFC-12, 28 percent; CFC-11, 23 percent; CCl_4, 13 percent; CFC-113, 6 percent). They are inert in the troposphere but photodissociate in the stratosphere and hence are a major source of stratospheric reactive chlorine. The CFCs are used as refrigerants, foam blowing agents and solvents. CCl_4 is used in the production of CFCs.

1.2.1 CFC-11 and CFC-12

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

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

Table 1-1 Updated global trends and tropospheric concentrations of source gases for 1989. Adapted from WMO (1990b).

Source gas	Concentration 1989 (pptv)	Increase 1989 pptv/year	Increase 1989 percent/year	Calibration uncertainty
CH_4	1689×10^3	$(12–14) \times 10^3$	0.7–0.8	±1%
H_2	515×10^3	$(2.7–3.7) \times 10^3$	0.5–0.7	?
N_2O	$(307–308) \times 10^3$	$(0.6–0.9) \times 10^3$	0.2–0.3	±1%
CO NH	$(100–150) \times 10^3$	$(0.4–1.2) \times 10^3$	0.3–1.0	±5%
SH	$(50–60) \times 10^3$	0	0	
CO_2	352.2×10^6	1.6×10^6	0.5	<0.1%
C_2H_6 NH			0.6–1.2	
CCl_2F_2	453	16.9–18.2*	3.7–4.0	±2%
CCl_3F	255–268	9.3–10.1	3.7–3.8	±1%
CCl_2FCClF_2	64	5.4–6.2	9.1	±10%
$CClF_2CClF_2$	15–20	≈1	≈6	
CCl_2FCF_3	≈5	≈0.3	≈6	
$CClF_3$	≈5			
CCl_4	107	1.0–1.5	1.2	±10%
CH_3CCl_3	135	4.8–5.1	3.7	±15%
$CHClF_2$	110	5–6	6–7	±10%
CH_3Cl	600			
$CHCl_3$	≈10			
CH_2Cl_2	≈35			
CCl_2CCl_2	≈30			
CH_2ClCH_2Cl	≈35			
$CHClCCl_2$	≈10			
CH_3Br	10–15	?		
CH_2Br_2	2–3			
$CHBr_3$	2–3			
CH_2BrCl	1–2			
$CHBr_2Cl$	1			
$CHBrCl_2$	1			
$C_2H_4Br_2$	1			
C_2H_5Br	2–3			
$CBrClF_2$	1.6–2.5	0.2–0.4	15	±15%
$CBrF_3$	1.8–3.5	0.4–0.7	20	±40%
COS	≈500	?		
Total Cl	3800	110	2.9	
Percent anthropogenic	≈80			
Total Br	40	0.9	2.3	
Percent anthropogenic	≈12 (halons only)			

*Data subject to revision; significantly lower trends may result (see text).

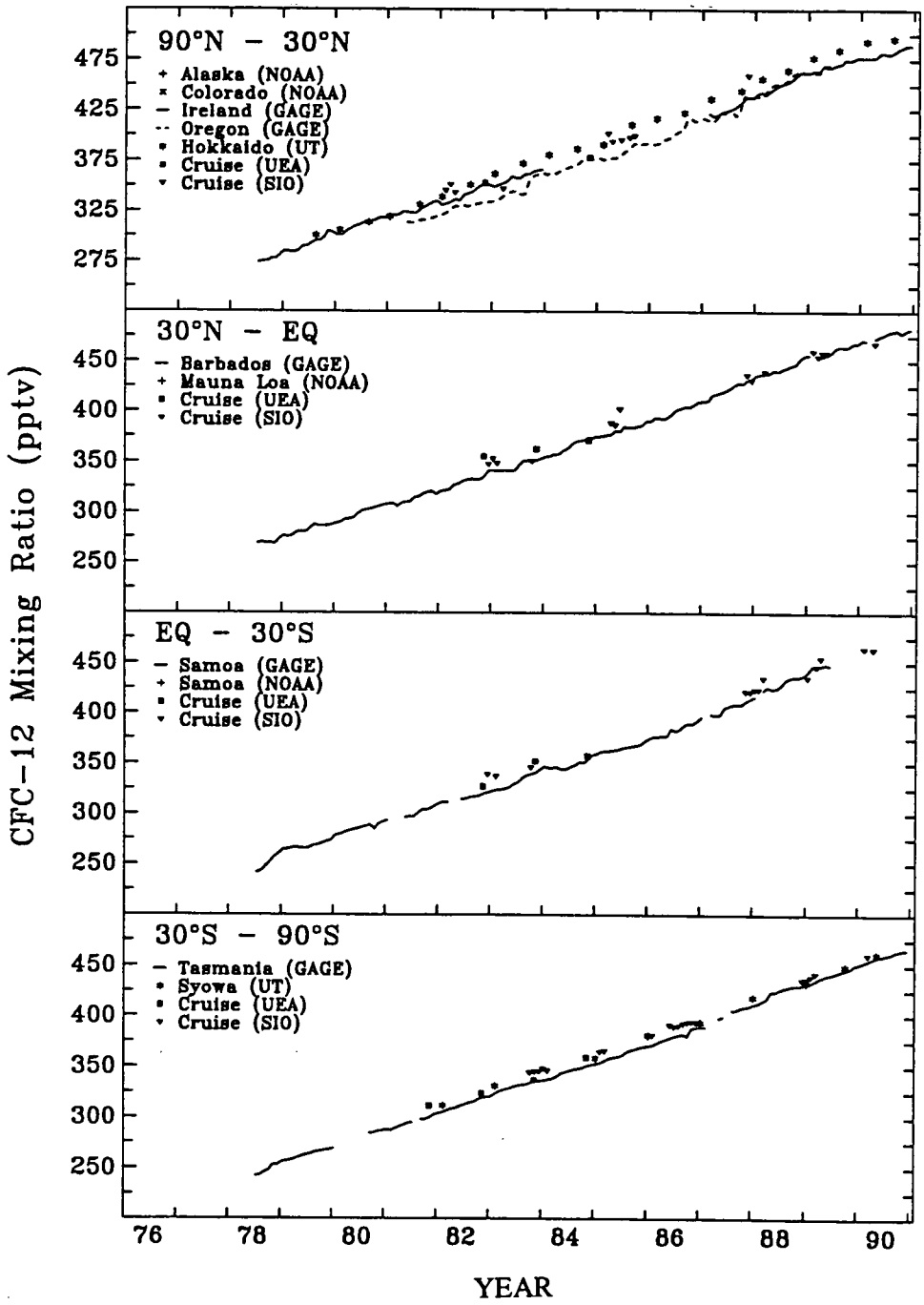

Figure 1-1 CFC-12 observations (pptv) in the four semihemispheres (NOAA: Thompson *et al.*, 1990; GAGE: Cunnold *et al.*, 1986; Prinn *et al.*, 1991b; UT: Makide *et al.*, 1987; Makide 1991). Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: NOAA, J. Elkins; GAGE, R. Prinn; UT, Y. Makide; UEA, S. Penkett; SIO, R. Weiss.

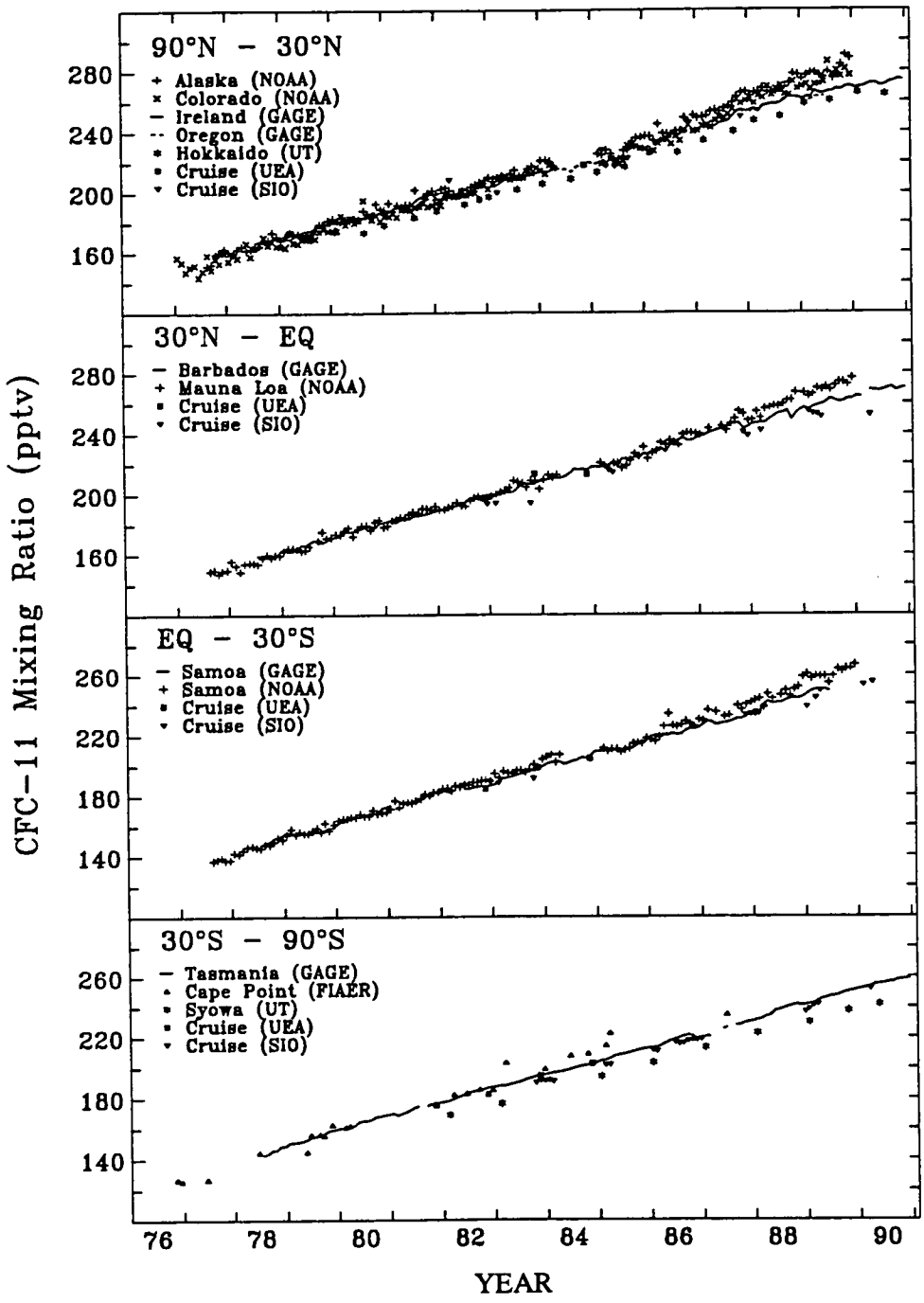

Figure 1-2 CFC-11 observations (pptv) in the four semihemispheres (NOAA: Thompson *et al.*, 1990; GAGE: Cunnold *et al.*, 1986: Prinn *et al.*, 1991b; UT: Makide *et al.*, 1987; Makide 1991) some of the data are unpublished and subject to revision. Data should not be used for further analysis without consulting the principal investigators: NOAA, J. Elkins; GAGE, R. Prinn; UT, Y. Makide; UEA, S. Penkett; SIO, R. Weiss; FIAER, H. Scheel.

lutely demonstrated by extensive, periodic internal comparisons of several original ALE–GAGE calibration gases and by a comparison of measurements made in 1978–1979 in the ALE–GAGE program in Tasmania with modern measurements on air archived from that period. These experiments limit the magnitude of a calibration drift component of the observed trend to about 0.1 percent per year. A possible CFC-12 calibration problem has been identified in the GAGE data, which are currently being reevaluated. Lower trends will probably result (D. Cunnold, GAGE–GIT, personal communication) although the changes are likely to be small.

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

In situ CFC-11 measurements (24 per day) have been made at Cape Point, South Africa, since 1980 (Scheel *et al.*, 1990; Brunke and Scheel, 1991). The 1989 annual mean CFC-11 concentration at Cape Point (34°S) was 256 pptv, increasing at 9.3±0.1 pptv per year or 3.6 percent per year in 1989 based on a linear regression. The data are reported in the original OGIST scale and are also shown in Figure 1-2. The 1989 mean CFC-11 concentration and trend at Cape Point in the GAGE scale (OGIST x 0.96) are 246 pptv and 9.0 pptv per year respectively, which compare well with the 1989 mean CFC-11 concentration and trend in Tasmania (GAGE program, 41°S), 247 pptv and 9.3±0.1 pptv per year respectively.

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

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

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

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

1.2.2 CFC-113

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

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

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

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

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

1.2.3 CFC-114 and CFC-114a

Rasmussen *et al.*, (1990) has reported growth rates for CFC-114 ($CClF_2CClF_2$) and CFC-114a (CCl_2FCF_3) from the OGIST global flask sampling network from 1979 to 1990 of approximately 6 percent per year. Absolute concentrations were not reported. There have been no new data reported for CFC-115.

1.2.4 Carbon Tetrachloride

In situ CCl_4 measurements have been made at the GAGE stations since 1978 (Simmonds *et al.*, 1988). The data (Figure 1-4) show a global mean 1989 concentration of 134 pptv, based on data from Ireland, Barbados, and Tasmania, and an increase over the entire record of 1.6±0.3 pptv per year, or 1.2 percent per year in 1989.

A similar CCl_4 increase has been observed from *in situ* measurements at Cape Point (1.7±0.1 pptv per year) over the period 1980–1990 (Figure 1-4). This program employs the same calibration scale as the GAGE program. The 1989 mean concentration (128 pptv) at Cape Point (32°S) is very similar to that observed (130 pptv) at Cape Grim, Tasmania (41°S). However *in situ* measurements in 1989 at Samoa (14°S) and the South Pole using the new NOAA–CMDL gravimetric calibration scale gave mean concentrations of 104 and 106 pptv respectively (Thompson *et al.*, 1990; Hall *et al.*, 1990), whereas GAGE measurements at Samoa in 1989 average about 132 pptv, suggesting that concentrations in the NOAA–CMDL scale are ≈20 percent lower than those in the GAGE scale.

Flask measurements of CCl_4 on Hokkaido, (40°–45°N) over the period 1979–1990 show an increase of 1.4±0.2 pptv per year (Makide *et al.*, 1987; Makide, 1991). A direct interlaboratory comparison between GAGE and Makide indicate that the GAGE CCl_4 scale is ≈20 percent higher than Makide (Y. Makide and P. Fraser, unpublished data).

Measurements of CCl_4 in the free troposphere over Europe and the North Atlantic during the period

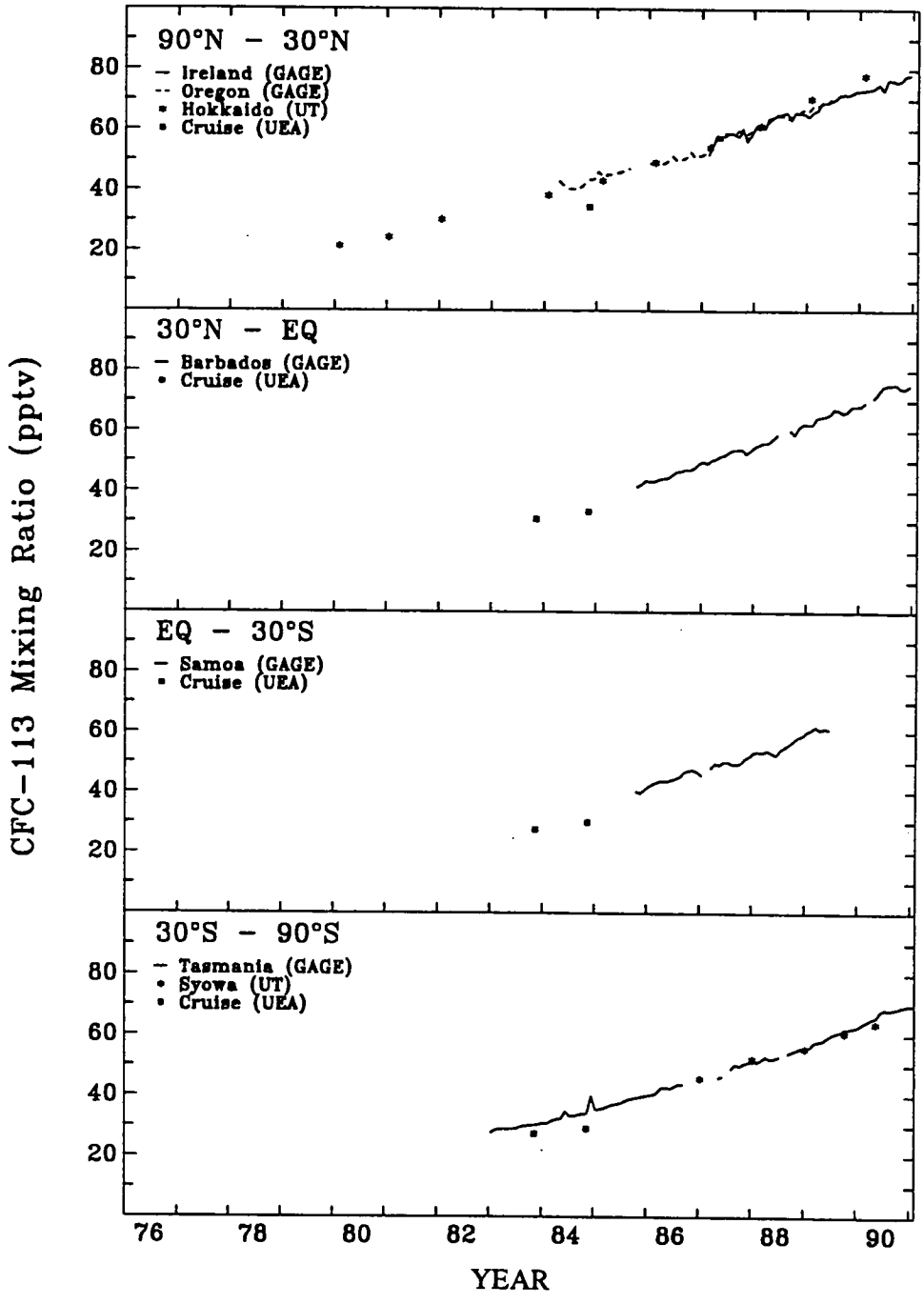

Figure 1-3 CFC-113 observations (pptv) in the four semihemispheres (GAGE: Fraser *et al.*, 1991; Prinn *et al.*, 1991b; UT: Makide, 1991). Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: GAGE, R. Prinn; UT, Y. Makide; UEA, S. Penkett.

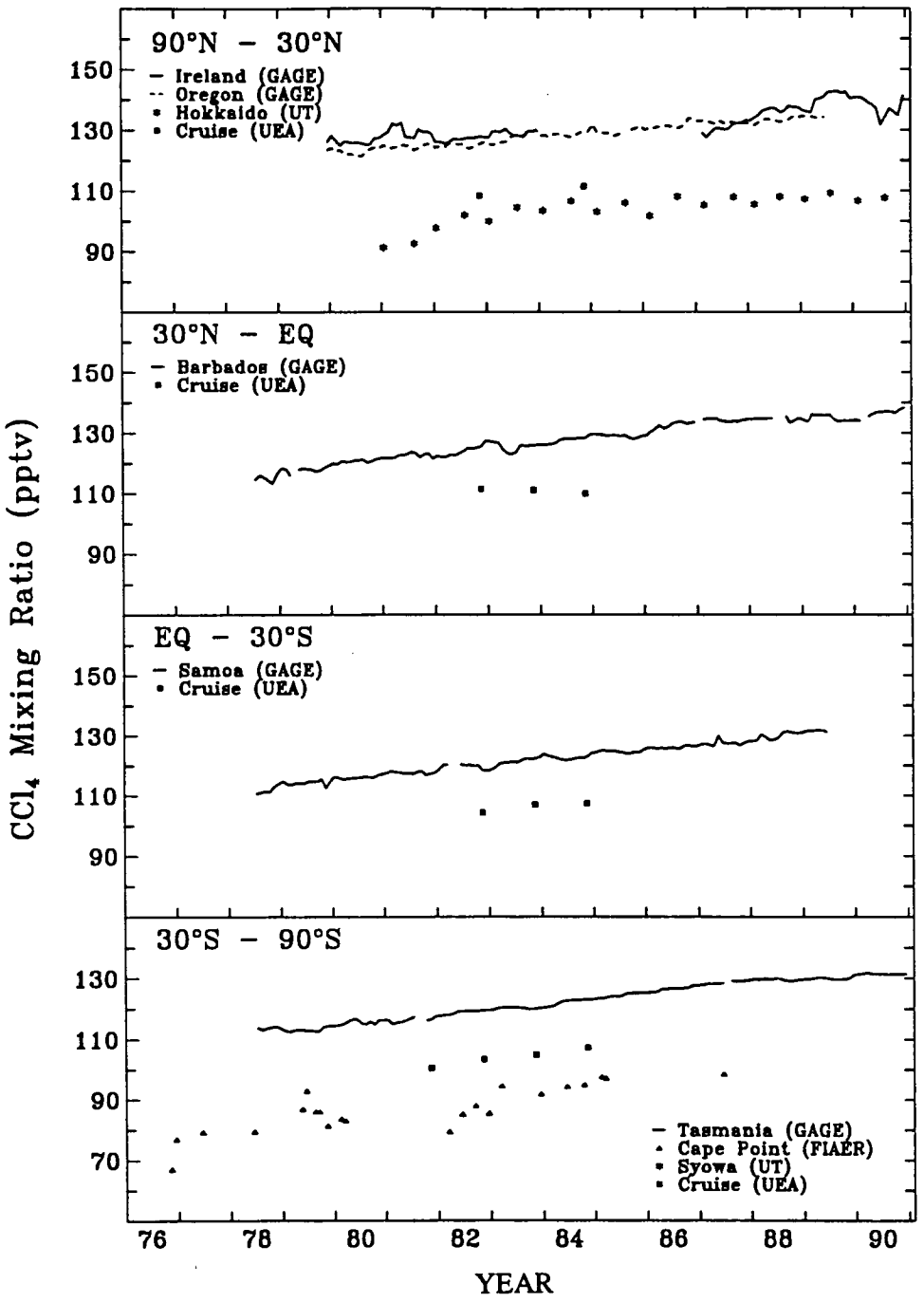

Figure 1-4 Carbon tetrachloride (pptv) in the four semihemispheres. (GAGE: Simmonds *et al.*, 1988; Prinn *et al.*, 1991b; UT: Makide *et al.*, 1987; Makide, 1991; CSIR-FIAER: Scheel *et al.*, 1990). Some of the data are unpublished and are subject to revision. Data should not be used for further analysis withou consulting the principal investigators: GAGE, R. Prinn; UT, Y. Makide; UEA, S. Penkett; FIAER, H. Scheel

1976–1987 show an increase of 2.0±0.3 pptv per year (Seiler and Scheel, 1991). These data are based on a Scott-Marrin calibration standard, which gives CCl_4 concentrations that are a factor of ≈1.15 lower than those based on the GAGE calibration.

Measurements of CCl_4 at Cape Grim (41°S) have been compared to CCl_4 measurements on the South Atlantic at similar latitudes and times, which were obtained using an independent calibration scale (UEA) (Penkett, 1991a). The Atlantic data were approximately 15 percent lower, which probably reflects the difference in calibration scales (*i.e.*, GAGE/UEA ≈1.15). A direct comparison of National Institute of Standards and Technology (NIST) and GAGE CCl_4 standards indicates that the GAGE/NIST ratio is ≈1.35 (Fraser, personal communication, 1991).

It would appear that five independent laboratories (UT, NOAA–CMDL, UEA, Fraunhofer Institute for Atmospheric Environmental Research (FIAER) (Scott-Marrin), and NIST) agree to within ±10 percent on CCl_4 calibration, and are ≈20 percent lower than GAGE.

1.3 METHYL CHLOROFORM AND HCFC-22

Methyl chloroform (CH_3CCl_3) and HCFC-22 ($CHClF_2$) are important trace gases in the global atmosphere. They constitute about 17 percent of the tropospheric anthropogenic organochlorine loading (CH_3CCl_3, 14 percent; $CHClF_2$, 3 percent) and both are partially removed from the atmosphere by reaction with OH. Assuming emissions and absolute abundances of these species are known, they can be used to calculate average tropospheric OH levels (for CH_3CCl_3, see Prinn *et al.*, 1987, 1992). Methyl chloroform is used as an industrial solvent and HCFC-22 is being increasingly used as a substitute for CFCs.

1.3.1 Global distributions and trends

Long-term, high-frequency measurements (4-12 per day) of CH_3CCl_3 have been made in Ireland, Oregon, Barbados, Samoa and Tasmania (Prinn *et al.*, 1987, 1991a) since 1978 as part of the ALE-GAGE program and on Hokkaido twice a year (10 days every 6 months) since 1979 and at Syowa Station in Antarctica (several times per year) (Makide *et al.*, 1987; Makide, 1991). January measurements made in the Pacific North West (PNW) of the United States and at the South Pole since 1975 have been published (Rasmussen and Khalil, 1986; Khalil and Rasmussen, 1990b). Mid-tropospheric CH_3CCl_3 data have been obtained by aircraft air sampling over Europe and the North Atlantic by FIAER since 1978 (Scheel *et al.*, 1988).

The available data are shown in Figure 1-5. Twelve years of ALE–GAGE CH_3CCl_3 data (July 1978 to June 1990) have recently been analyzed (Prinn *et al.*, 1992) showing a global trend of 5.5±0.2 pptv per year or 4.4±0.2 percent per year (mid-1984). The 1989 global mean concentration was 150.0 pptv (based on data from Ireland, Barbados, and Tasmania), and the 1989 increase, based on a linear regression, was 3.7 percent. The free tropospheric data over Europe and the North Atlantic (1978–1987) show a trend of 5.2±0.8 pptv per year or 4.5 percent per year in 1984 (Scheel *et al.*, 1988; Seiler and Scheel, 1991). The Hokkaido data (Makide *et al.*, 1987; Makide, 1991) show an increase of 4 pptv per year over the period 1980–1990 (2.7 percent in 1989) and 5 pptv per year over the period 1987–1990 (3.4 percent in 1989). The concentrations of CH_3CCl_3 observed on Hokkaido are about 15 percent lower than in Ireland or Oregon, although these differences could be due to different calibration scales (see 1.3.2).

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

HCFC-22 data have been regularly obtained from the PNW region of the U.S. and from the South Pole (Rasmussen *et al.*, 1980; Khalil and Rasmussen, 1981; Rasmussen and Khalil, 1982, 1983). The PNW data from 1976 to 1981 showed concentrations increasing by about 12±1 percent per year, with an absolute concentration uncertainty of ±10 percent. Combined PNW–South Pole data for 1979–1987 have recently been reported (Khalil and Rasmussen, 1990b), which show a concentration in January 1987 of 105 pptv increasing by 6.4±0.3 pptv per year or 6.1 percent in January 1987. Observations from Cape Grim (1984–1987), show a mean concentration and increase in 1987 of 91 pptv and 6.5±0.3 pptv per year, or 7.1±0.3 percent per year (Fraser *et al.*, 1989). These data are all in the same scale (OGIST)

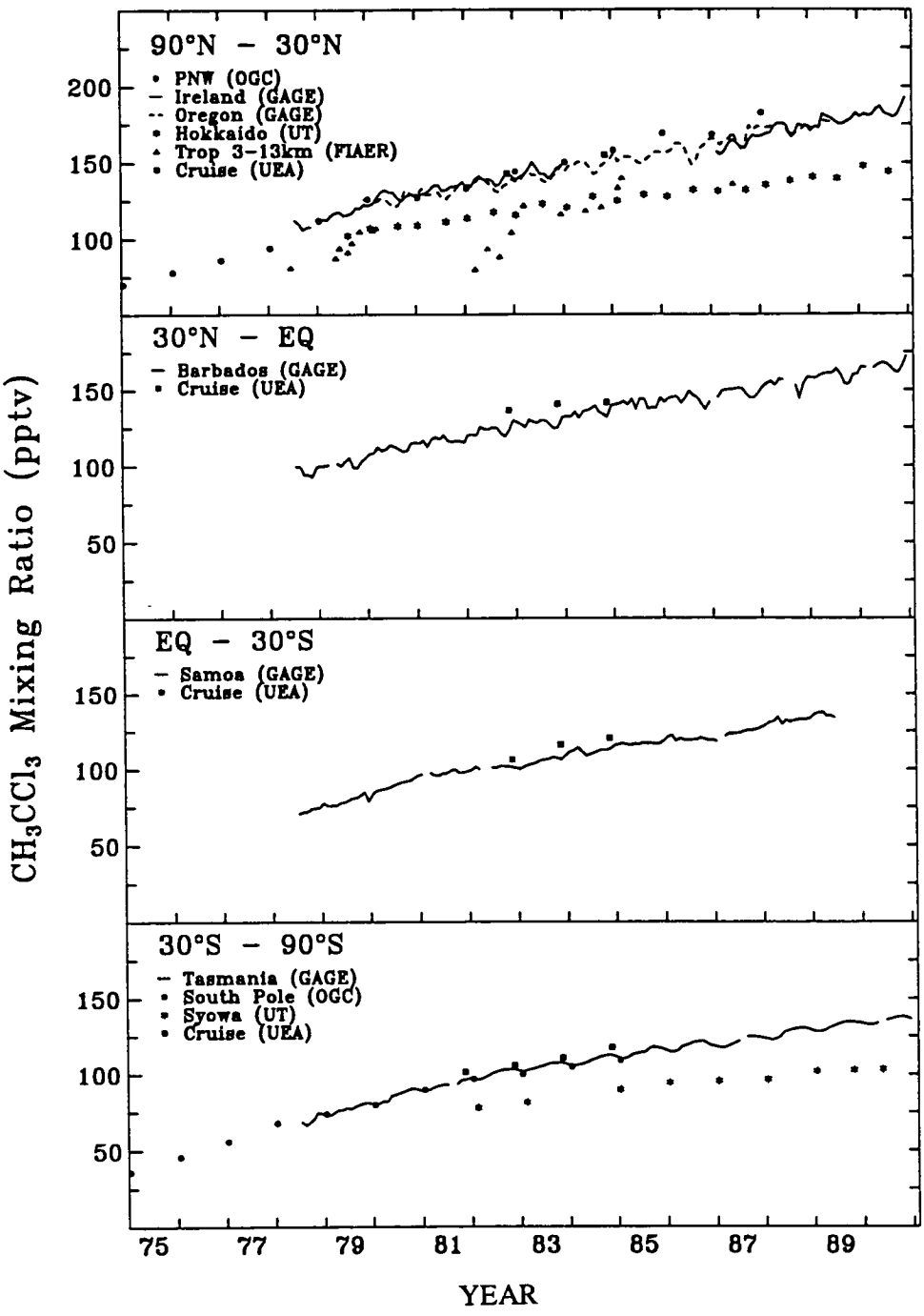

Figure 1-5 Methyl chloroform observations (pptv) in the four semihemispheres (GAGE: Prinn *et al.*, 1991, 1992, UT: Makide *et al.*, 1987 Makide, 1991. FIAER: Scheel *et al.*, 1988; Seiler and Scheel, 1991. OGIST: Rasmussen and Khalil, 1986; Khalil and Rasmussen, 1990b.) Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: GAGE, R. Prinn; UT, Y. Makide; UEA, S. Penkett; FIAER, H. Scheel.

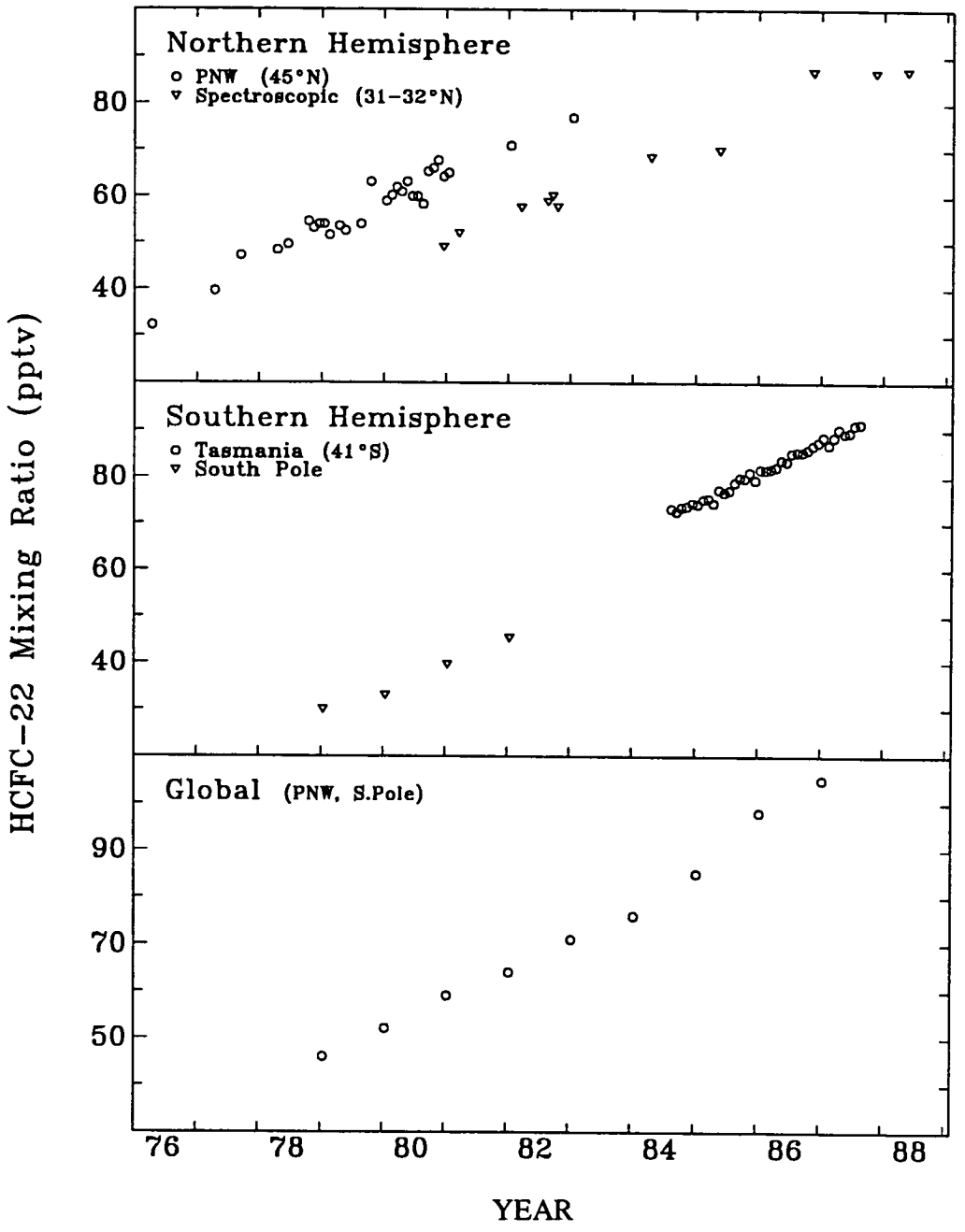

Figure 1-6 Northern Hemispheric, Southern Hemispheric, and global HCFC-22 observations (pptv) (PNW, South Pole: Khalil and Rasmussen, 1981; Rasmussen and Khalil, 1982, 1983; spectroscopic: Rinsland *et al.*, 1989, 1990; Tasmania: Fraser *et al.*, 1989; global: Khalil and Rasmussen, 1990b).

and are shown in Figure 1-6. The OGIST and UEA independent HCFC-calibration 22 scales agree to within 5 percent (Rasmussen *et al.*, 1980).

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

1.3.2 Methylchloroform Calibration

The absolute calibration of CH_3CCl_3 measurements in the GAGE program is based on the OGIST standard (Khalil and Rasmussen, 1984a). Unfortunately, there have not been any published comparisons of independently derived CH_3CCl_3 standards. A preliminary and as yet unpublished comparison between the GAGE and UT CH_3CCl_3 standards suggests that the latter are lower by ≈25 percent (UT/GAGE = 0.75) (Y. Makide and P. Fraser, unpublished data).

A new gravimetric CH_3CCl_3 standard has been prepared by NOAA–CMDL (Butler *et al.*, 1991). No direct comparisons have been made between this standard and the GAGE standard, but an indirect comparison can be made from observations by both groups in the Southern Hemisphere in early 1990 (Butler *et al.*, 1991; Prinn *et al.*, 1991a). This comparison suggests that the NOAA–CMDL standard is about 10 percent lower than the GAGE standard (NOAA–CMDL/GAGE = 0.9). Shipboard measurements of CH_3CCl_3, based on an independent calibration, have been made on the North and South Atlantic (Penkett, 1991a) between 1981 and 1984. A comparison of ALE–GAGE data at similar latitudes and times indicates that the UEA standard is about 5 percent higher than the GAGE standard (UEA/GAGE = 1.05). Thus, the current range of CH_3CCl_3 measurements based on four independent standards (GAGE, UT, NOAA–CMDL, UEA) would appear to be ±15 percent. The average of the four standards is ≈10 percent lower than GAGE.

The long-term stability of the OGIST CH_3CCl_3 standard has been possibly but not absolutely demonstrated by extensive, periodic internal comparisons of several original ALE–GAGE calibration gases and by a comparison of measurements made in 1978–1979 in the ALE–GAGE program in Tasmania with modern measurements on air archived from that period. These experiments limit the magnitude of a calibration drift component of the observed trend to about 0.2 percent per year, comparable to the uncertainty in the long-term trend due to measurement variability (Prinn *et al.*, 1992).

1.3.3 Methylchloroform Lifetime and the Global OH Abundance

A three-dimensional model has been used to compute tropospheric OH levels from observations of CH_4, CO, O_3, and NO_x (Spivakovsky *et al.*, 1990a) and used to simulate the global distribution of CH_3CCl_3 (Spivakovsky *et al.*, 1990b). The computed OH fields result in a model CH_3CCl_3 lifetime of 5.5 years. The observed CH_3CCl_3 annual cycle south of 25°S is dominated by seasonal changes in OH (CH_3CCl_3 sink), whereas the seasonal variation of CH_3CCl_3 in the tropics and at northern mid–latitudes are dominated by the effects of transport.

The measured ALE–GAGE trends of CH_3CCl_3 have been combined with industrial emission estimates (Midgley, 1989) to deduce a globally averaged CH_3CCl_3 lifetime of 5.7 (+0.7, –0.6) years) and an average tropospheric OH concentration of (8.7±1.0) x 10^5 radicals per cm^3 (Prinn *et al.*, 1992).

Theoretical (Wine and Chameides, 1990) and observational (Butler *et al.*, 1991) studies have suggested that the ocean is a significant sink for CH_3CCl_3. The data of (Butler *et al.* 1991) imply that OH levels computed from CH_3CCl_3 data are 5–10 percent too high if the oceanic sink is ignored. Incorporating an oceanic sink into the GAGE CH_3CCl_3 inversion study results in a lower average OH level of (8.1±0.9) x 10^5 radicals per cm^3 (Prinn *et al.*, 1992).

The ALE–GAGE CH_3CCl_3 trend implies that the globally averaged OH levels have been increasing over the period 1978–1990 by 1.0±0.8 percent per year (Prinn *et al.*, 1992). The deduced positive OH trend is qualitatively consistent with predicted changes in tropical tropospheric OH and O_3 driven by tropical biomass burning (Keller *et al.*, 1991). This possible trend in OH has major implications for other trace gases that are primarily removed by reaction with OH, *e.g.*, CH_4, CO, HCFC-22 and other HCFCs and HFCs.

1.3.4 HCFC-22 lifetime

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

1.4 OTHER CHLORINATED SPECIES

1.4.1 Methyl Chloride

There have been no data, further to (WMO, 1990a), reported on the global distribution of methyl chloride (CH_3Cl). A global average background concentration of ≈600 pptv is assumed.

1.4.2. Chloroform

Chloroform measurements have been made regularly at Cape Grim as part of the OGIST flask sampling program and as part of the GAGE *in situ* measurement program. The GAGE data have been calibrated with respect to a NIST SRM (Fraser, 1991). The global background concentration in 1989 was ≈10 pptv, based on the previously reported ratio of Northern to Southern Hemispheric measurements (Khalil and Rasmussen, 1983b). Approximately 40 percent of the $CHCl_3$ source required to maintain the observed global concentration (400 million kg per year) is anthropogenic (Khalil and Rasmussen, 1983b). Termite mounds were found to contain elevated levels of $CHCl_3$, which were calculated to emit 100 million kg per year (Khalil *et al.*, 1990).

1.5 HALONS AND OTHER BROMINATED SPECIES

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

The most abundant is methyl bromide (CH_3Br), which has both natural and anthropogenic sources. The main natural sources of CH_3Br are oceanic biological processes (mainly algal), where it is formed with other hydrogen-containing molecules, such as CH_2Br_2, $CHBr_3$, CH_2BrCl, and $CHBrCl_2$. However, measurements of CH_3Br made over the Atlantic Ocean show a marked interhemispheric gradient, with average concentrations of 15 pptv and 10 pptv being recorded in the Northern and Southern Hemispheres respectively (Penkett *et al.*, 1985). This argues for a substantial land-based source, which could well be anthropogenic. The source strength required to produce the observed abundance is 100 million kg per year, whereas the annual anthropogenic production is about 20 million kg (SORG, 1990). There may be other unaccounted sources of anthropogenic CH_3Br.

Observational data records of sufficient frequency and duration to determine possible trends in atmospheric bromine species are rare. The available halon data from the OGIST flask sampling network up to 1986 were recently summarized (WMO, 1990a), which suggested global mean concentrations and rates of increase of 1.7 and 2.0 pptv and 12 and 15 percent per year respectively for $CBrClF_2$ and $CBrF_3$. Thompson *et al.* (1990) have reported NOAA–CMDL shipboard data in 1987 and 1989 of 1.6 and 1.8 pptv, increasing at 8 and 25 percent per year respectively for $CBrClF_2$ and $CBrF_3$.

Rasmussen, *et al.* (1990) has recently revised the global growth rates from the OGIST flask network to be ≈15 and ≈20 percent per year respectively for $CBrClF_2$ and $CBrF_3$, but absolute concentrations were not reported. Based on the 1986 data and the latest growth rates, the concentrations expected in 1989 for $CBrClF_2$ and $CBrF_3$ would be 2.5 and 3.5 pptv respectively. Singh *et al.* (1988) reported tropospheric

concentrations for $CBrClF_2$ and $CBrF_3$ at the mid-latitudes of the Northern Hemisphere in 1987 of 2.0 and 1.3 pptv respectively. The $CBrClF_2$ data compare favorably with the OGIST Northern Hemispheric data (WMO, 1990a), but the $CBrF_3$ data are ≈50 percent lower. These data from three independent laboratories (OGIST, NOAA–CMDL, and Max Planck Institute for Aeronomy, or MPIA) suggest that the uncertainties in calibration of $CBrClF_2$ and $CBrF_3$ are ≈±15 percent and ≈±40 percent respectively.

1.6 CARBONYL SULPHIDE

Chlorine-catalyzed O_3 destruction may be enhanced by heterogeneous processes on the ubiquitous stratospheric aerosol layer (Brasseur *et al.*, 1990). In times of low volcanic activity this stratospheric aerosol layer (sulphate) is maintained by an upward flux of gaseous sulphur precursors, mainly carbonyl sulphide (COS), which are either oxidized or photolyzed in the stratosphere (Crutzen, 1976), while volcanic injections supply sulphur to the stratosphere mainly as sulphur dioxide (SO_2) during individual volcanic eruptions.

COS is the most abundant sulphur gas in the remote atmosphere. Global background concentrations of COS are 510±10 pptv (Khalil and Rasmussen, 1984b). The major sources are the oceans (20–40 percent), via the photooxidation of organic material (Ferek and Andreae, 1984), anthropogenic activities (20 percent), soils (20 percent), biomass burning (10 percent) and the oxidation of carbon disulphide (CS_2) (30 percent), while the major sinks are vegetation (≈80 percent), tropospheric oxidation (≈10 percent) and stratospheric loss (≈10 percent) (Khalil and Rasmussen, 1984b; Servant, 1989). Estimates of the atmospheric lifetime range from 2 to 6 years.

1.7 NITROUS OXIDE

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

Nitrous oxide is a long-lived atmospheric species, with a lifetime in excess of 150 years (Prinn *et al.*, 1990), whose dominant source is believed to be denitrification in aerobic soils, which has a significant anthropogenic component (deforestation and the use of nitrogenous fertilizers). Biomass burning and fossil fuel combustion are now believed to be only small N_2O sources, although biomass burning may affect subsequent soil N_2O releases (Anderson *et al.*, 1988; Prinn *et al.*, 1990; IPCC, 1990). The oceans are significant sources of N_2O, which vary considerably with location and ocean circulation processes (Butler *et al.*, 1989; IPCC, 1990). The major sinks for N_2O are stratospheric photodissociation and photooxidation.

1.7.1 Atmospheric Distributions and Trends

There are several long-term measurement programs studying N_2O. Shipboard and ground-based measurements have been regularly made by Scripps Institution for Oceanography (SIO) since 1976 (Weiss, 1981; WMO, 1990a). NOAA–CMDL and ALE–GAGE have operated independent five-station networks covering both hemispheres since 1977 and 1978 respectively (Thompson *et al.*, 1990; Prinn *et al.*, 1990). Long-term N_2O measurement programs have been carried out at Cape Point since 1983 (Brunke *et al.*, 1990; Scheel *et al.*, 1990) and in the PNW of the United States and at the South Pole since 1975 (Rasmussen and Khalil, 1986; Khalil and Rasmussen, 1990b). Mid-tropospheric N_2O data have been obtained by aircraft air sampling over Japan (33°–38°N) since 1983 by Meteorological Research Institute (MRI) (Hirota *et al.*, 1988; Hirota and Sasaki, 1991) and over Europe and the North Atlantic by FIAER since 1979 (Scheel *et al.*, 1988).

The available data are shown in Figure 1-7 divided into the four semihemispheres, as well as global data derived by averaging spline fits to the individual CMDL and ALE–GAGE station data sets. From the SIO data (1976–1987) (not shown) a global average concentration and increase (1986) of 304.8 ppbv and 0.61±0.04 ppbv per year or 0.20 percent per year have been deduced (WMO, 1990a). The NOAA–CMDL data (1977–1989) show a global concentration and increase for 1989 of 308.5 ppbv and 0.64±0.06 ppbv per year or 0.21 percent per year (Thompson *et al.*, 1990). The ALE–GAGE data (1978–1989) show a global concentration in 1988 of 307.2 ppbv and an increase (1978–1988) of 0.25–0.31 percent per year (Prinn *et al.*, 1990). The 1989 global mean was 307.0 ppbv (mean of Northern Hemisphere (Ireland, Barbados) and Southern Hemisphere (Tasmania) (Prinn *et al.*, 1991). The Cape Point data (1983–1988) show

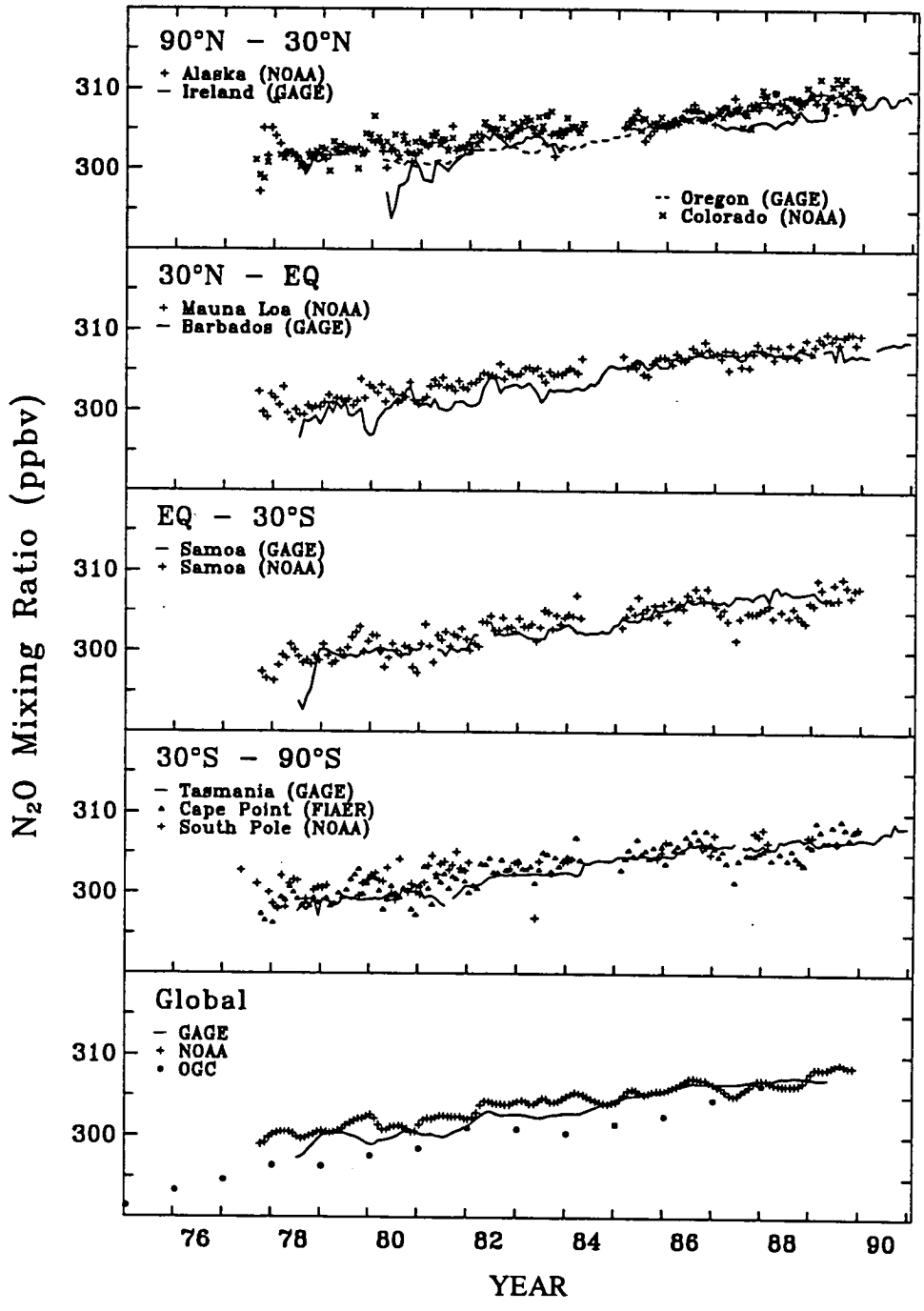

Figure 1-7 Nitrous oxide observations (ppbv) in the four semihemispheres (NOAA: Thompson *et al.*, 1990. OGIST: Khalili and Rasmussen, 1990b) Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: NOAA, J. Elkins; GAGE, R. Prinn; FIAER, H. Scheel.

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

The mid-tropospheric N_2O data over Japan show an average increase (1983–1989) of 1.7±0.2 ppbv per year (Hirota and Sasaki, 1991). The free tropospheric data over Europe and the North Atlantic between 1979 and 1987 show an annual average increase of 0.5 ppbv per year or 0.16 percent per year (1987) (Scheel *et al.*, 1988). Spectroscopic observations of N_2O from Kitt Peak between 1979 and 1985 place an upper limit on the growth rate of 0.3 percent per year (Wallace and Livingston, 1990b).

1.7.2. Global Nitrous Oxide Budgets

The ALE–GAGE data have been interpreted (Prinn *et al.*, 1990), using inverse theory and a nine-box model of the global atmosphere, to show that the global distributions and trends are consistent with the hypothesis that stratospheric photodissociation is the major sink for N_2O and that the cause of the N_2O trend appears to be a combination of a growing tropical source (probably tropical land use) and a growing northern mid-latitude source (fertilizer and fossil fuel use). The N_2O budget that best fits the ALE–GAGE observations (not a unique solution) is shown in Table 1-2, together with the budget produced for the IPCC (IPCC, 1990).

The IPCC budget indicates that there are probably unaccounted for or underestimated N_2O sources, while the (Prinn *et al.*) budget is essentially balanced. The difference between the two budgets is largely due to the significant biomass burning-tropical land clearing term in the latter, resulting from large post-burn, postclearing N_2O emissions (Anderson *et al.*, 1988; Luizao *et al.*, 1989; Prinn *et al.*, 1990). The global emissions of N_2O due directly to biomass burning alone have been recently reassessed as less than 2 Tg (N_2O) per year (Cofer *et al.*, 1991) or even less than 1 Tg (N_2O) per year (Crutzen and Andreae, 1990; Hao *et al.*, 1991).

Table 1-2 The global N_2O budget, Tg (10^{12}g) (N_2O) per year (IPCC, 1990; Prinn *et al.*, 1990; Sanhueza, 1991).

	IPCC (1990)	Prinn *et al.* (1990)	Sanhueza (1991)
Sinks			
photodissociation	11–20	13–16	11–20
atmospheric growth	5–7	6–7	5–7
Total	16–27	19–23	16–27
Sources			
oceans	2–4	4	2–4
soils – tropical	4–6	6	4–9
temperate	1–2	1	<1–3
fossil fuel use	<1	2	<1–1
biomass burning	<1	5	<1–2
fertilizer use	<1–4	2	<1–5
adipic acid production	<1		<1–1
Total	7–16	20	8–25

A revised N_2O budget, prepared for IPCC (Sanhueza, 1991) is also given in Table 1-2. The estimates were updated using new information on tropical soil fluxes (Sanhueza *et al.*, 1990; Matson *et al.*, 1990), temperate forest soil fluxes (Bowden *et al.*, 1990), detailed evaluations of cultivated soils (Bouwman, 1990; Eichner, 1990), and new estimates from biomass burning (Lobert *et al.*, 1990; Cofer *et al.*, 1991). Recent results have confirmed that the N_2O emissions from stationary combustion sources are very low (De Soete, 1989; Linak *et al.*, 1990; Sloan and Laird, 1990; Yokoyama *et al.*, 1991).

Other, possibly globally significant, N_2O sources have been identified since the IPCC review and are included in Table 1-3. The worldwide production of nylon could contribute $\leq$ 1 Tg (N_2O) per year (Thiemens and Trogler, 1991), and mobile combustion sources $\approx$0.6 Tg per year (De Soete *et al.*, 1989). The revised N_2O budget still indicates that there are unidentified and/or underestimated N_2O sources.

Some possible candidates are the use of legume pastures as nitrogenous fertilizers, which account for 15 percent of Australian N_2O emissions (Galbally *et al.*, 1992) and the significant, but unidentified, emissions of N_2O (2–3 Tg [N_2O] per year), possibly from stationary sources in Europe (Prather, 1988; Simmonds and Derwent, 1991).

1.8 METHANE

Methane is an important trace gas in the global atmosphere because it absorbs infrared radiation, thus impacting on climate. Methane is involved in tropospheric chemistry via OH and O_3 budgets, and it impacts on stratospheric chemistry as a source of hydrogen (H_2) and H_2O and as a sink for stratospheric chlorine. Methane is produced from a variety of anaerobic processes and is primarily removed by reaction with OH in the troposphere.

1.8.1 Atmospheric Distributions and Trends

There are several long-term CH_4 measurement programs. Ground-based measurements at globally distributed sites have been regularly made by NOAA–CMDL (USA) since 1983 (Steele *et al.*, 1987; Lang *et al.*, 1990a, b), by CSIRO (Australia) since 1978 (Fraser *et al.*, 1986a), by UCI (USA) since 1978 (Blake and Rowland, 1988), and by OGIST (USA) since 1978 (Khalil and Rasmussen, 1983a; 1990a). Long-term CH_4 measurement programs have been carried out at Cape Point, South Africa, since 1983 by CSIR (South Africa)–FIAER (Germany) (Brunke *et al.*, 1990; Scheel *et al.*, 1990), in the PNW and at the South Pole since 1975 (Rasmussen and Khalil, 1986), and at Tsukuba, Japan, since 1985 (Hirota *et al.*, 1989). Mid-tropospheric CH_4 data have been obtained by aircraft air sampling over southeast Australia (Fraser *et al.*, 1984, 1986a) since 1980 and over Europe and the North Atlantic by FIAER since 1979 (FIAER, Scheel *et al.*, 1988).

Selected available CH_4 data are shown in Figure 1-8, divided into the four semi-hemispheres and the published CH_4 trends are summarized in Table 1-3.

The rate of methane increase has slowed during the last decade, as observed at Cape Grim, Tasmania, (1978–1983: >20 ppbv per year; 1983–1990: 12±2 ppbv per year; (Steele *et al.*, 1987; WMO, 1990; Fraser, 1991) and in Antarctica (1983: 13.6 ppbv per year; 1988: 10.4 ppbv per year; (Steele *et al.*, 1989). The global University of California at Irvine (UCI) and Oregon Graduate Center (OGC) data have also shown a decline in CH_4 growth rate, from 19–25 ppbv per year (1981–1983) to 11–20 ppbv per year (1984–1987), with most of the decline in the growth rate occurring in 1983–1984 (Khalil and Rasmussen, 1990a). The observed growth rates as a function of time for the global OGIST and UCI and CSIRO Southern Hemispheric networks are shown in Figure 1-9. The data confirm high growth rates during 1978–1982 (17–21 ppbv per year), which have since declined to 8–13 ppbv per year (1988–1990). Satisfactory explanations for this rapid decline in CH_4 growth rates have yet to emerge.

Prinn *et al.* (1992) have calculated from industry emission estimates and trend observations of CH_3CCl_3 that OH levels in the tropical troposphere are increasing about 1 percent per year. If correct, this has important implications for the CH_4 budget. It suggests that the increasing levels of OH are as important as the approach to equilibrium in determining the slowing down in the CH_4 growth rate. It also allows sources to grow at 1–2 percent per year, rather than the 0–1 percent per year required if OH is constant.

Stevens (1988) has noted that the change in atmospheric CH_4 growth rate was accompanied by changes in its ^{13}C composition. This was true in both the Northern and Southern Hemispheres, where there were

Table 1-3 Global and regional CH_4 trends (ppbv per year, percent per year) from various observational networks.

Network (period)	Region/Location	Increase		Year	Reference
		ppbv per year	percent per year		
Ground–based Measurements					
NOAA–CMDL	Global	12.8	0.8	1984	1–4
(since 1983)	Global	12.9±0.1	0.8	1986	
	South Pole	11.9±0.1	0.7	1988	
CSIRO	Southern	18±2	1.3	1981	3,5,6
(since 1978)	Hemisphere	18±1	1.2	1984	
		11.9±0.2	0.7	1986	
UCI	Global	16±1	1.0	1987	7–9
(since 1978)		12–13	0.7–0.8	1990	
OGIST	Pacific N.W., U.S.	17.5±1.3	1.1	1985	3,10–12
(since 1978)	South Pole				
	Global	13.1±0.1	0.8	1986	
	Global	16.6±0.4	1.0	1988	
1960–1980	Global	13±3	0.8	1979	
FIAER	Cape Point,	10.3±0.3	0.7	1984	13
(since 1983)	South Africa				
MRI	Tsukuba,	9.0	0.5	1987	14
(since 1985)	Japan				
Free Tropospheric Measurements					
CSIRO	S.E. Australia	20±4	1.2	1981	3,5,6
(since 1980)		19±1	1.2	1984	
		12±1	0.8	1986	
FIAER	Europe and	12.7	0.8	1987	15
(since 1987)	North Atlantic				
Total Column Measurements					
1951–1986	Jungfraujoch, Switzerland		0.7		16
1979–1985	Kitt Peak, U.S.		1.1		17
1979–1989			1.0		18

References: 1, Steele *et al.*, 1987; 2, Steele *et al.*, 1989; 3, WMO, 1990a; 4, Novelli *et al.*, 1990; 5, Fraser *et al.*, 1984; 6, Fraser *et al.*, 1986a; 7, Blake and Rowland, 1988; 8, Rowland, 1990; 9, Rowland and Blake, 1991; 10, Rasmussen and Khalil, 1986; 11, Khalil and Rasmussen, 1990a; 12, Khalil *et al.*, 1989; 13, Brunke *et al.*, 1990; 14, Hirota *et al.*, 1989; 15, Scheel *et al.*, 1988; 16, Zander *et al.*, 1989a; 17, Wallace and Livingston, 1990a; 18, Thompson *et al.*, 1990.

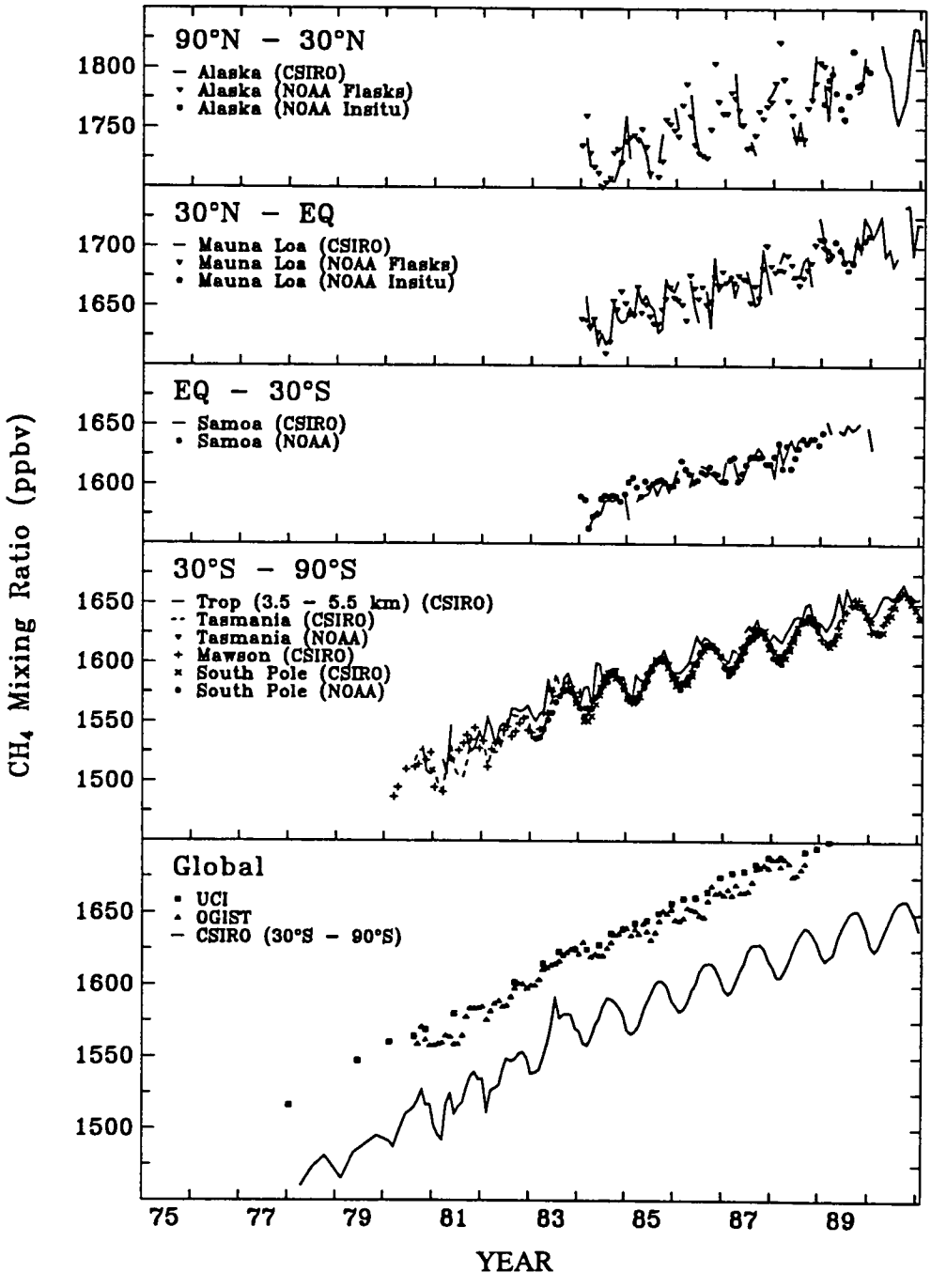

Figure 1-8 Methane observations (ppbv) in the four semihemispheres (NOAA: Steele *et al.*, 1987; Lang *et al.*, 1990a, b. CSIRO: Fraser *et al.*, 1986a, 1990; Fraser, 1991. OGIST: Khalil and Rasmussen, 1990a. UCI: Blake and Rowland, 1988; Rowland, 1990; Blake and Rowland 1991). The CSIRO (30°S–90°S) data are averages of Cape Grim (41°S) and Mawson (67°S) data. Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: CSIRO, P. Fraser; UCI, D. Blake.

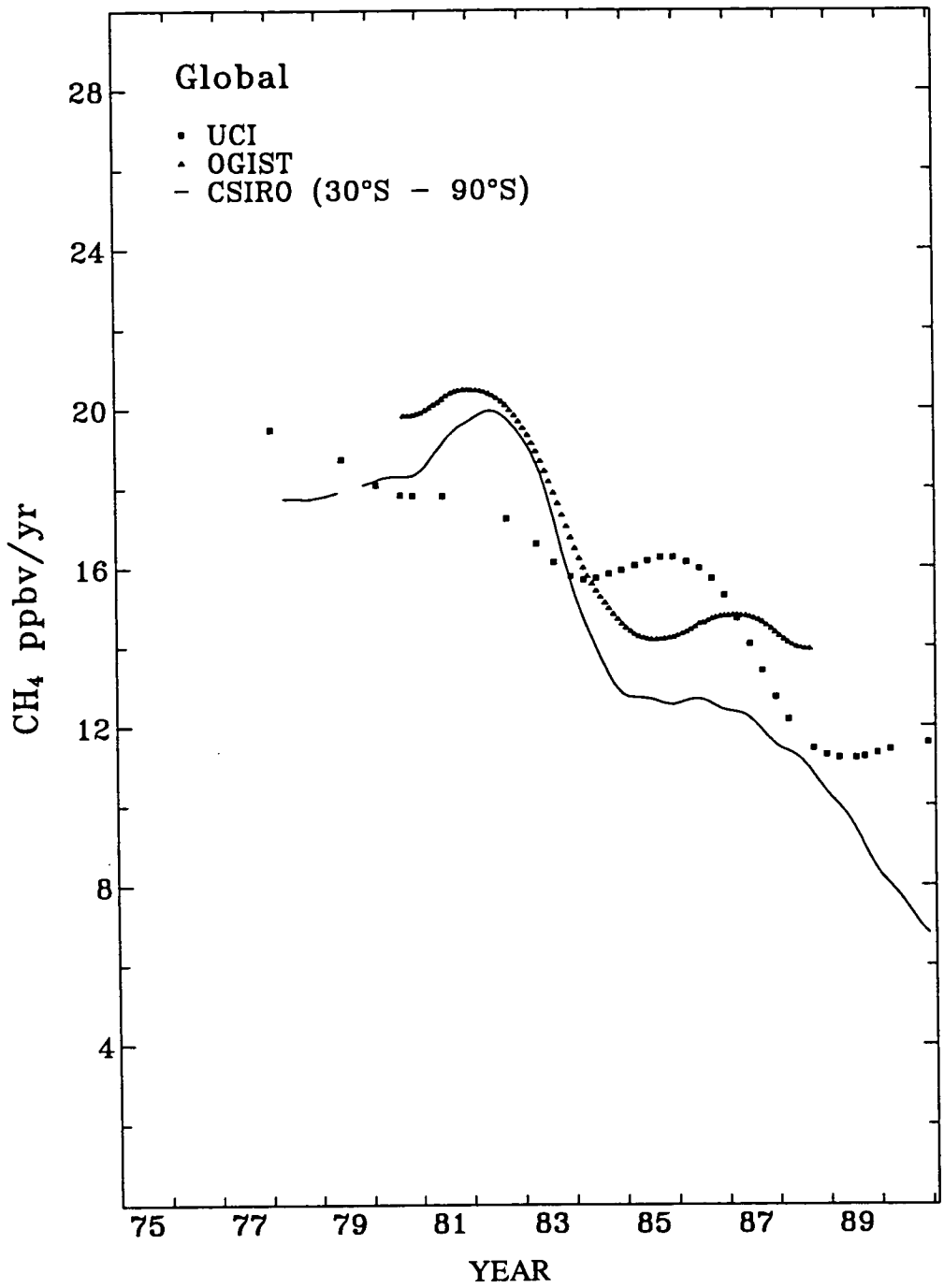

Figure 1-9 The global and Southern Hemispheric CH_4 trends from 1978–1990. The trends are obtained from spline fits to the long–term CH_4 data records (Blake and Rowland, 1988, 1991; Rowland, 1990; Khalil and Rasmussen, 1990a; Fraser *et al.*, 1986a, 1990; Fraser, 1991).

reductions in the ^{13}C depletion. These changes have been tentatively interpreted as indicating that there were changes in the source distribution of CH_4 (probably in the Northern Hemisphere) that were not of anthropogenic origin. It was suggested that there may have been a decrease in the flux of isotopically light (more ^{13}C-depleted) CH_4 of natural origin, such as that from wetlands.

Recent results from a high-accumulation-rate ice core (Etheridge *et al.*, 1992) show that there have been significant variations in the CH_4 growth rate over the period 1840–1980, with accelerating growth from 1890 (≤0.2 percent per year) to 1925 (0.5 percent per year), approximately constant growth from 1925 to 1950 (≈0.5 percent per year), followed by accelerating growth from 1950 (0.5 percent per year) to 1975 (≈1 percent per year). This pattern appears to correlate with the changing production rates of fossil fuels (Keeling, 1973; Marland and Rotty, 1984), perhaps indicating a significant role for this CH_4 source in determining global CH_4 growth rates.

1.8.2 Methane Sinks

The dominant removal process for atmospheric CH_4 is reaction with OH. A new measurement (Vaghjiani and Ravishankara, 1991) of the rate coefficient for the reaction of OH and CH_4 found it to be approximately 25 percent lower than reported previously, implying that the OH-CH_4 sink is approximately 420 Tg per year.

The magnitude of the OH-CH_4 sink is estimated from models whose OH fields are calibrated by the estimated releases and observed trends of methyl chloroform (CH_3CCl_3, see 1.3.3). A further uncertainty in the magnitude of the OH-CH_4 sink has resulted from theoretical (Wine and Chameides, 1990) and observational (Butler *et al.*, 1991) studies suggesting a biological or physical sink for CH_3CCl_3 in oceanic surface waters, which, if confirmed, could further reduce calculated OH levels (and the OH-CH_4 sink) by 10–20 percent.

Modeling studies suggest that OH levels, and hence the relative strength of the CH_4 sink, in preindustrial times were higher than at present. Studies of the ratio of formaldehyde (HCHO), a CH_4 oxidation product, to CH_4 in polar ice cores suggest that OH levels in preindustrial times were 30 percent higher than at present (Staffelbach *et al.*, 1991).

Studies in Arctic, temperate, and tropical environments have firmly established the importance of a global soil sink for atmospheric CH_4 (Steudler *et al.*, 1989; Keller *et al.*, 1990; Mosier *et al.*, 1991; Crill, 1991; Whalen and Reeburgh, 1990). However, there is considerable uncertainty associated with the magnitude of the soil sink for methane (5–60 Tg per year) (Born *et al.*, 1990). The destruction of CH_4 in soils is a biological process that is sensitive to both climatic variations and land use changes. Recent CH_4 soil flux measurements indicate that changes in land use or enhanced nitrogen input to soils by fertilization and/or deposition of atmospheric nitrogen are decreasing the CH_4 uptake by soils (Scharffe *et al.*, 1990; Mosier *et al.*, 1991).

1.8.3 Methane Sources

A recently identified CH_4 source that has not been considered previously is emissions from waste water and animal waste treatment facilities (40–65 Tg per year) (Harriss, 1991). Animal wastes contribute 20–30 Tg per year (Casada and Shafley, 1990). The landfill source may be ameliorated by identified high CH_4 oxidation rates in landfill cover soils (Whalen *et al.*, 1990). The preliminary data on CH_4 emissions from landfills, waste water treatment and animal wastes indicate a total emission of 85±20 Tg per year from anthropogenic waste management systems (Harriss, 1991).

Studies of the ^{14}C and ^{13}C isotopic composition of atmospheric CH_4 have been used to evaluate the contribution to total emissions made by fossil sources. Three independent estimates are (21±3) percent (Whalen *et al.*, 1989), 25 percent (Manning *et al.*, 1990; Lowe *et al.*, 1991) and 16 percent (Quay *et al.*, 1991). The latter value, combined with the reduction in the overall source inferred from the new estimate of the OH-CH_4 sink, would constrain the total fossil source to 90±10 Tg per year. Current estimates of CH_4 emissions from the production and use of oil, natural gas, and coal are compatible with this estimate for the total fossil source. Thus, the contributions of fossil sources such as CH_4 hydrate destabilization and the decomposition of old peat are apparently small.

For ^{13}C, differing amounts of depletion are found for different CH_4 sources. Bacterially produced CH_4, such as that from wetlands, rice paddies, ruminants, and termites, is typically more highly depleted in ^{13}C than is nonbacterial CH_4, such as that produced in biomass burning and in emissions of natural gas. Consideration

of the observed ^{13}C depletion in CH_4 sources together with that of atmospheric CH_4 and the ^{12}C–^{13}C fractionation factor associated with the reaction of CH_4 and OH indicates that bacterial CH_4 makes up some 70 percent of CH_4 sources (Quay *et al.*, 1991).

Methane emission rates from Chinese rice paddies (total emissions: 30 Tg per year, Khalil *et al.*, 1991) were found to be 4–10 times higher than from U.S. and European rice fields. Matthews *et al.* (1991) calculate Chinese and Indian CH_4 emissions from rice production of approximately 20 and 30 Tg per year respectively, assuming a global rice CH_4 source of 100 Tg per year (Fung *et al.*, 1991). By contrast, recent results from the major rice producing areas of India and Japan (Parashar *et al.*, 1991; Mitra, 1991; Yagi and Minami, 1990) indicate emissions that are not significantly different from the U.S. and European data. The Indian data indicate an annual CH_4 flux of only 3–4 Tg per year, an order of magnitude lower than calculated above. Large rice emissions from China and India are consistent with a global rice source of about 100 Tg per year, which is in agreement with constraints imposed by atmospheric observations (Fung *et al.*, 1991, see below). Based on the latest Indian data, Sanhueza (1991) has adopted a lower estimate of CH_4 emissions from rice agriculture (60 Tg per year) for the IPCC review of global CH_4 emissions. R. Cicerone (private communication) estimates that the uncertainty in global emissions from rice is still very large (≈ a factor of seven).

1.8.4 Global Methane Budgets

The NOAA global CH_4 data base have been interpreted with a three-dimensional model incorporating geographic and seasonal emission distributions of the major CH_4 sources and sinks (Fung *et al.*, 1991). Various source and sink scenarios were tested, constrained by the observed geographic and seasonal CH_4 distributions and the observed ^{13}C and ^{14}C composition of atmospheric CH_4. A preferred, but not necessarily unique, budget for CH_4 was derived, which is shown in Table 1-4 along with that derived for IPCC (IPCC, 1990) and also recently by Crutzen (1991), Harriss

Table 1-4 The global CH_4 budget (Tg (CH_4) per year). The numbers in parentheses are the range of uncertainties in sources and sinks. Adapted from: Fung *et al.* (1991); IPCC (1990); Crutzen (1991); Harriss (1991); Sanhueza (1991).

	Fung *et al.* (1991)		IPCC (1990)		Crutzen (1991)		Harriss (1991)		Sanhueza (1991)	
Source										
Wetlands	115	(100–200)	115	(100–200)	115	(165––265)	110	(60–160)	115	(100–200)
Rice	100	(60–170)	110	(25–170)	100		100	(50–150)	60	(200–100)
Animals	80	(65–100)	80	(65–100)	80	(65–100)	80	(65–95)	80	(65–100)
Fossil fuels	75	(50–95)	80	(45–100)	95	(75–115)	90	(80–100)	95	(80–120)
Biomass burning	55	(50–100)	40	(20–80)	30	(15–45)	30	(15–45)	30	(20–80)
Land fills	40	(30–70)	40	(20–70)	50	(30–70)	85	(65–105)	85	(65–105)
Termites	20	(10–200)	40	(10–100)	20	(10–100)			20	(5–50)
Oceans	10	10 (5–20)	10	(5–20)					10	(5–20)
Others	5	10 (0–120)	5				50	(25–75)	10	(1–30)
Total	500	(380–950)	525	(290–960)	505	(370–720)	545	(360–730)	505	(360–805)
Sink										
Chemical loss	450	(405–495)	500	(400–600)	430	(350–510)	430	(345–515)	430	(350–510)
Soils	10	(5–60)	30	(15–45)	30	(15–45)	30	(15–45)	30	(15–45)
Atmospheric Increase	45	(40–50)	45	(40–50)	45	(40–50)	45	(40–50)	45	(40–48)
Total	505	(450–605)	575	(455–695)	505	(405–605)	505	(400–610)	505	(405–605)

(1991), and Sanhueza (1991). The global CH_4 budget is an underdetermined problem where there are more sources and sinks than there are observations to constrain them. The largest uncertainties in CH_4 emissions are associated with landfills, tropical swamps, rice fields, biomass burning, and termites, due to a lack of direct measurements of fluxes in regions were these sources are concentrated.

In contrast to the IPCC CH_4 budget, there is now fairly good agreement between CH_4 sources and sinks plus atmospheric accumulation. This is due largely to the revised (25 percent lower) atmospheric consumption of CH_4 by OH radicals (Vaghjiani and Ravishankara, 1991). However, there still remains considerable uncertainty associated with the global methane budget. Recent estimates of methane emissions from animal wastes and waste water treatment are included in Table 1-3 only in the Harriss (1991) and Sanhueza (1991) budgets, under landfills. A possibly large methane source from asphalt (Sackett and Barber, 1988), now appears to be less than 1 Tg per year (Tyler *et al.*, 1990).

1.9 HYDROGEN

Oxidation of H_2 in the stratosphere may affect stratospheric O_3 by supplying H_2O vapor to the stratosphere, in addition to that derived from H_2O transported from the troposphere and CH_4 oxidation.

1.9.1 Global Distribution and Trends

Measurement of H_2 in air samples collected in the OGIST global flask sampling program between 1985 and 1989 shows that the concentration of H_2 has increased by 3.2±0.5 ppbv per year (Khalil and Rasmussen, 1990e). The global average concentration in 1989 was ≈515 ppbv, based on the global trend and the 1988 average concentration. The concentration of H_2 in the Southern Hemisphere is about 3 percent higher than in the Northern Hemisphere. The Cape Grim data (1984–1987) from the OGIST network have been reported separately (Fraser *et al.*, 1989).

1.9.2 Sources and Sinks

The global source and sink of H_2 is estimated to be about 90 Tg per year (Khalil and Rasmussen, 1990e), the major sources being CH_4 oxidation (30 percent), oxidation of NMHCs (25 percent), anthropogenic activities (20 percent) and biomass burning (15 percent). The major sinks are removal by soils (85 percent) and oxidation by OH (15 percent). The increasing concentration of H_2 in the atmosphere is probably due to growing sources, for example, the observed CH_4 trend may account for 50 percent of the observed H_2 trend. The higher H_2 concentrations in the Southern Hemisphere compared to the Northern Hemisphere have been interpreted as indicating that the soil sink is the dominant cause of the interhemispheric difference. The observed seasonality in the Southern Hemisphere possibly reflects the local production by CH_4 and NMHC oxidation, while the seasonality in the Northern Hemisphere may reflect the seasonality in the soil sink (Khalil and Rasmussen, 1989).

1.10 CARBON MONOXIDE

Carbon monoxide (CO) is an important trace gas in the troposphere because it plays significant roles in controlling the chemistry of ozone production and hydroxyl radical destruction in the lower atmosphere. It directly affects the oxidizing capacity of the lower atmosphere and can thus influence the concentrations of other important trace gases such as CH_4, CH_3CCl_3, and the HCFCs.

1.10.1 Atmospheric Distributions and Trends

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

However, over continental sites in both hemispheres, even in clean air, CO concentrations are elevated and highly variable. For example, in the Southern Hemisphere average concentrations of about 100 ppbv over tropical Brazil are typical (Kirchhoff *et al.*, 1989; Kirchhoff and Marinho, 1989).

Remote sensing from space provides a global picture of CO spatial variability (Reichle *et al.*, 1990), indicating large biomass burning sources over South America and tropical Africa, which presumably influence the local production of tropospheric ozone, which is subsequently transported over a significant portion of the Southern Hemisphere (Watson *et al.*, 1990). Long-term CO data are not yet available from space platforms.

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

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

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

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

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

1.10.2 Carbon Monoxide Calibration

There has been significant progress in the calibration of CO measurements. (Weeks *et al.* 1989) have compared an ambient concentration OGIST calibration gas used in the CSIRO CO program to a dynamically-diluted NIST (formerly NBS) SRM (#2612a, 9.7 ppmv CO in air) and found that ambient levels of CO in the Southern Hemisphere in the NIST scale are ≈30–40 percent higher than those reported in the OGIST scale (≈35–55 ppbv). The CSIRO data reported here (Figure 1-10) are in the NIST scale. Note that there is now good agreement between FIAER and CSIRO measurements at similar latitudes in the Southern Hemisphere. The FIAER CO scale has been found to be within 4 percent of the NIST scale (Brunke *et al.*, 1990). The OGIST scale has recently been revised such that CO concentrations are now reported 20 percent higher than previously (Khalil and Rasmussen, 1990d). A comparison of NIST (U.S.) and National Physical Laboratory (NPL) (U.K.) gravimetric standards indicates agreement to within 0.2 percent at a range of concentrations from 10 ppmv to 8 percent (Hughes *et al.*, 1991).

Novelli *et al.* (1991) at NOAA–CMDL have prepared two series of gravimetric standards of CO in air at 25 to 1,000 ppbv, from pure CO as well as from a NIST SRM at 9.7 ppmv. The two sets of standards

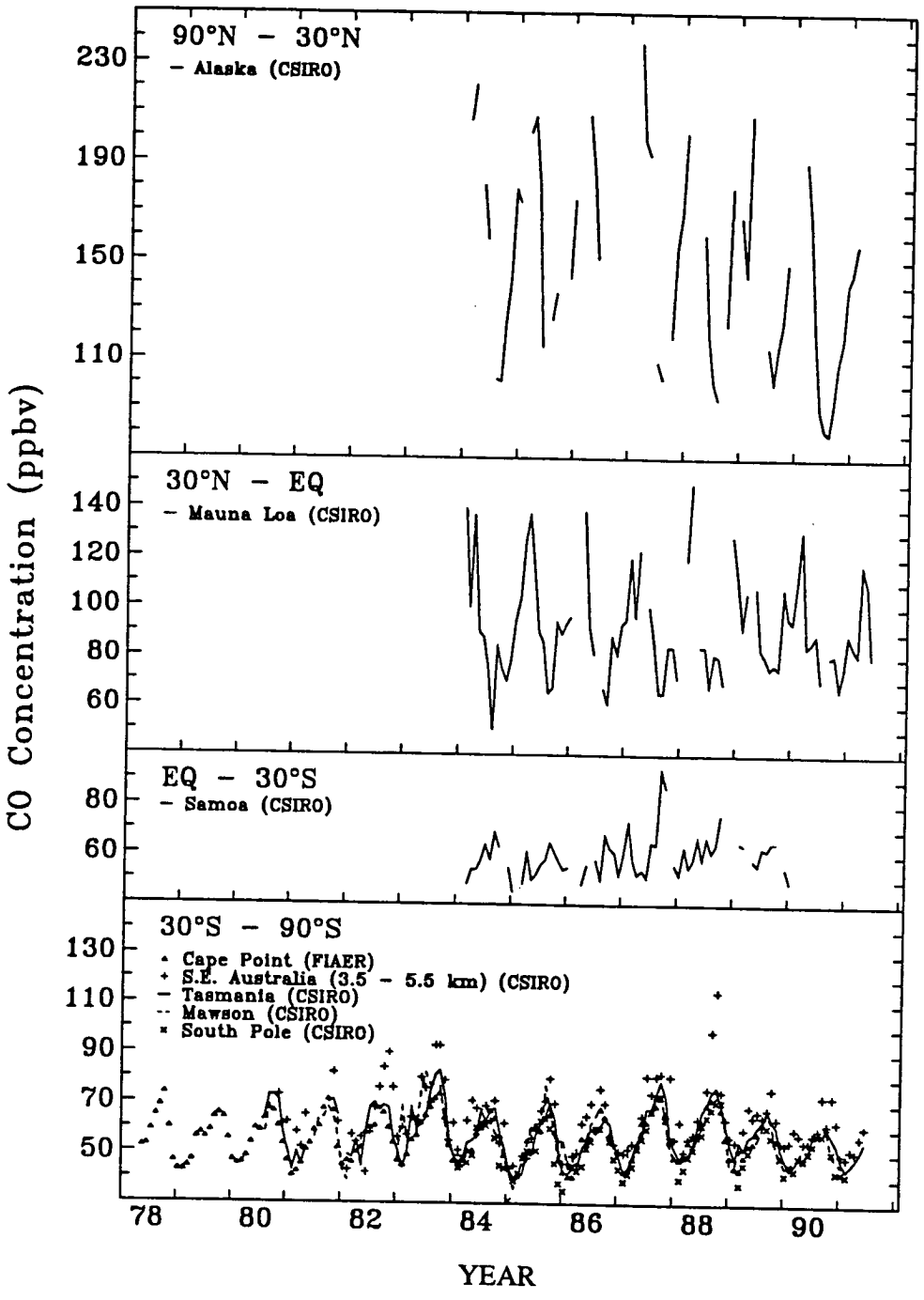

Figure 1-10 Carbon monoxide observations (ppbv) in the four semihemispheres. All data are from the CSIRO global flask network (Fraser *et al.*, 1986a, b; Fraser, 1991), except Cape Point (CSIR-FIAER: Brunke *et al.*, 1990; Scheel *et al.*, 1990). Some of the data are unpublished and are subject to revision. Data should not be used for further analysis without consulting the principal investigators: CSIRO, P. Fraser; FIAER, H. Scheel.

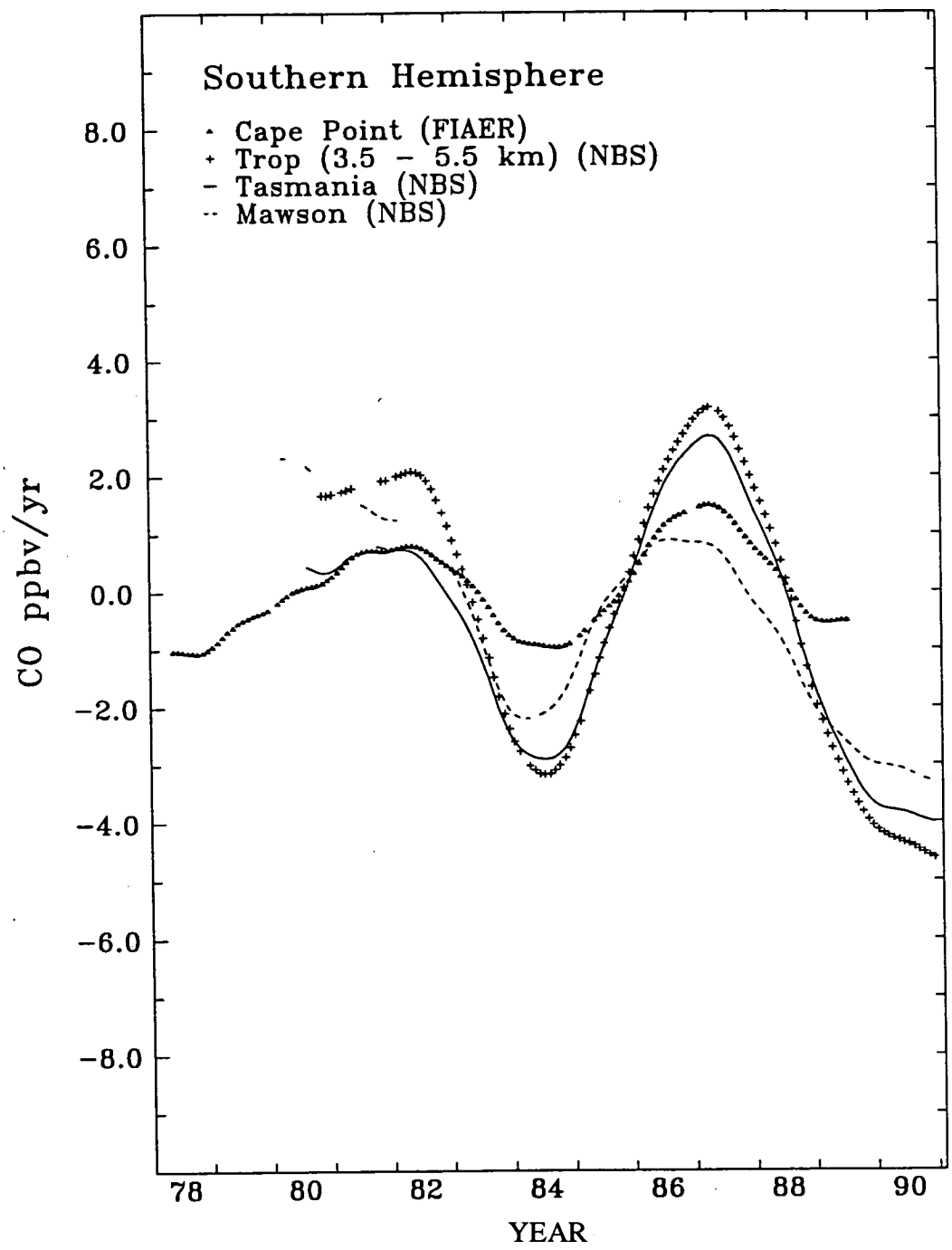

Figure 1-11 The Southern Hemispheric CO trends from 1978–1990. The trends are obtained from spline fits to the long-term CO data records (CSIRO: Fraser *et al.*, 1986a, b; Fraser, 1991. CSIR-FIAER: Brunke *et al.*, 1990; Scheel *et al.*, 1990)

agree to within 1 percent. Comparison of the OGIST and NOAA–CMDL scales at CSIRO showed that CO concentrations determined using the NOAA–CMDL scale are ≈25 percent higher than those obtained in the OGIST scale (before the 20 percent revision).

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

1.10.3. Global Carbon Monoxide Budgets

At present, there are several uncertainties in evaluating the sources and sinks of atmospheric CO. Carbon monoxide concentrations show a large degree of spatial (Reichle *et al.*, 1990) and temporal (Khalil and Rasmussen, 1988) variability, especially in the Northern Hemisphere over continental regions, which has not yet been adequately described by observational data. This presents serious problems in budget sensitivity studies when trying to match observations and model results (Fraser *et al.*, 1986b). The various CO concentration data sets reported to date in the literature are probably not known to better 10 percent in an absolute sense. According to Lelieveld and Crutzen (1991), the oxidation of formaldehyde (HCHO) in the liquid phase does not produce CO but CO_2 directly. Thus, the fraction of CH_4 and higher NMHCs that produce CO during the oxidation process need to be reevaluated.

Despite these uncertainties in evaluating CO budgets, there have been several attempts to produce global budgets for CO (Table 1-5). The total emissions of CO are probably between 2,000 and 3,000 CO Tg per year, with as much as $^2/_3$ being produced from anthropogenic activities, combustion processes (biomass (30 percent) and fossil fuel (20 percent)) being the dominant sources.

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

Table 1-5 The global CO budget, Tg per year.

	WMO (1986)	Logan (1990)	Seiler and Conrad (1987)		Khalil and Rasmussen (1990d)		Crutzen and Zimmerman (1991)
Sources							
Primary							
Fossil fuel	440	440	640	(440–840)	500	(400–1000)	500
Biomass burning	700	660	1,000	(400–1600)	680	(340–1400)	600
Vegetation		80	80	(50–100)	100	(50–200)	
Oceans	50	150	100	(10–190)	40	(20–80)	
Secondary							
NMHC oxidn	680	210	900	(400–1300)	690	(300–1400)	600
CH_4 oxidn	610	790	600	(300–900)	600	(400–1000)	630
Total	2480	2,330	3,320	(1,600–4,930)	2,600	(2,000–3,000)	2,330
Sinks							
OH reaction	1,910 (1,200–2,600)	2,020	2,000	(1,400–2,600)	≈2200	2,050	
soils	260	390	390	(150–530)	≈250	280	
stratosphere				110 (80–140)		≈100	
accumulation	20						
Total	2,190 (1,420–2,960)	2,410	2,500	(1,630–3,270)	≈2,550	2,330	

burning source are not readily available and the CO levels in urban areas of the developed countries appear to have declined over the past decade due to cleaner combustion processes (IPCC, 1990). The possibility of increasing levels of OH radical (Prinn *et al.*, 1991a) also complicates the prediction of CO trends.

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

1.11 NON-METHANE HYDROCARBONS (NMHCs)

NMHCs could possibly play a significant role in determining the OH radical concentration in the remote marine boundary layer (Bonsang *et al.*, 1988; Donahue and Prinn, 1990) and act as a significant source of CO. Because of their role in OH chemistry, NMHCs are important in assessing the significance of the OH sink for CH_4, CO, CH_3CCl_3, as well as the HCFCs and HFCs.

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

- relatively long-lived (lifetimes > week), where the highest concentrations (up to 3 ppbv for ethane (C_2H_6)) are observed in the middle to high northern latitudes;
- more reactive (lifetimes between 12 hours and a week), such as C_2-C_5 alkenes, whose concentrations exhibit significant temporal and latitudinal variability from <0.1 ppbv in remote areas to a few ppbv close to source regions;
- extremely short-lived (lifetimes of hours) such as terpenes or isoprene whose local concentrations only may reach about 10 ppbv close to their sources.

With the exception of C_2H_6, trends in the atmospheric concentrations of NMHCs have not been established. Recently (Ehhalt *et al.*, 1991) have reported a secular trend in the tropospheric concentration of C_2H_6 over the Northern Hemisphere of 0.9±0.3 percent per year, based on spectroscopic observations made at Jungfraujoch in 1951 and from 1984 to 1988, probably due to anthropogenic activities such as the use of fossil fuels and biomass burning.

1.11.1 Sources and Sinks for NMHCs

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

It has been generally accepted that the dominant loss mechanism for most NMHCs is reaction with the hydroxyl radical (OH). Other oxidants capable of removing hydrocarbons are ozone (O_3), the nitrate radical (NO_3), and chlorine atoms (Cl). Unsaturated hydrocarbons react rapidly with O_3 and NO_3 such that the atmospheric lifetimes of isoprene for removal by OH, O_3, and NO_3 are 18 hours, 1.2 days, and 20 hours respectively; for a terpene such as α-pinene the lifetimes are respectively 3.4 hours, 4.6 hours, and 2 hours (Corchnoy and Atkinson, 1990). It has also been proposed that chlorine atoms may remove large proportions of some saturated hydrocarbons such as ethane and propane (Singh and Kasting, 1988). This appears to be much less likely now after the findings of low HCl concentration (the source of the Cl atoms over the ocean) (Harris *et al.*, 1991).

To improve our understanding of the role of NMHCs in the tropospheric OH chemistry, a global observational data base of the unsaturated hydrocarbons (up to C_6) at the 1 pptv level is required, both in the atmosphere and surface ocean waters, as well as concurrent O_3, CO, and UV flux observations (Donahue and Prinn, 1990).

1.12 CARBON DIOXIDE

Next to H_2O vapor, CO_2 is the most important greenhouse gas in the atmosphere. Increasing concentrations of CO_2 are predicted to cause a warming of the troposphere and a cooling of the stratosphere, the latter resulting directly in increased levels of stratospheric O_3, or indirectly, through the formation of stratospheric aerosols, reduced levels of stratospheric O_3.

1.12.1 Atmospheric Distributions and Trends

There are several long-term measurement programs for CO_2 in the remote atmosphere. Recent publications from the NOAA–CMDL laboratory describe the results from *in situ* (Mauna Loa, Thoning *et al.*, 1989; Samoa, Waterman *et al.*, 1989) and flask observations (Conway *et al.*, 1988). Data up to 1989 are summarized in Novelli *et al.* (1990).

Concentrations in the Northern Hemisphere are typically 2–3 ppmv higher than in the Southern Hemisphere of CO_2, although the difference between the hemispheres shows substantial interannual variation. The global average CO_2 concentration and increase in 1989, based on the NOAA–CMDL *in situ* data from Barrow, Mauna Loa, Samoa, and the South Pole, was 352.2 ppmv and 1.6 ppmv per year respectively (Novelli *et al.*, 1990). The global average growth rate shows considerable variation from year to year, with values as high as 2.6 ppmv per year (1987–1988) and as low as 0.4 ppmv per year (1981–1982). The long-term growth rate is increasing.

Like CH_4, the observed change in CO_2 amounts has been accompanied by a change in its ^{13}C composition. CO_2 has become more depleted in ^{13}C as isotopically light (more ^{13}C-depleted) CO_2 is added to the lighter pool of atmospheric CO_2 (Kaye *et al.*, 1989).

Variations in atmospheric CO_2 are correlated with El Niño-Southern Oscillation (ENSO) events (Keeling *et al.*, 1989). Some clues to the cause of this correlation may be found in $^{13}C/^{12}C$ ratios of atmospheric CO_2, which allow CO_2 of terrestrial and marine origin to be distinguished. The $^{13}C/^{12}C$ data to date are somewhat contradictory (Keeling *et al.*, 1989; Francey *et al.*, 1990), so that a wide range of CO_2 fluxes associated with ENSO events are possible.

1.12.2 Sources and Sinks of CO_2

The extent to which the terrestrial biota contribute to long-term changes in atmospheric CO_2 has long been a contentious question in carbon cycle studies. Inversion calculations (two-dimensional model), using surface atmospheric CO_2 observations (Enting and Mansbridge, 1989, 1991; Tans *et al.*, 1989), and three-dimensional model studies, supplemented by analysis of surface atmospheric and oceanic partial pressure data (Tans *et al.*, 1990), concluded that there is a large, previously unidentified sink for CO_2 in the Northern Hemisphere, probably biotic uptake. More recently, it has been appreciated that the Tans *et al.* (1990) analysis neglects a natural cycle of CO_2 taken up by the terrestrial biota, transported into the oceans via rivers and then outgased into the atmosphere to close the cycle (Sarmiento and Siegenthaler, 1991). The existence of this cycle represents a correction of perhaps 0.6 Gt to the net ocean uptake calculated by Tans *et al.* (1990). In addition, Enting and Mansbridge (1991) noted that the role of CO in the atmospheric budget implies a correction of about 0.25 Gt to budgets based in interpreting the spatial distribution of CO_2. (The correction needs to be added to southern sinks and subtracted from northern sinks.) The effect of these corrections is to bring the ocean fluxes estimated by Tans *et al.* (1990) into much better agreement with ocean uptake based on global-scale carbon cycle modeling. However, this still implies the need for some biotic uptake of comparable magnitude to the carbon release from deforestation. In particular, estimates of the spatial distribution of CO_2 sources show a tropical source comparable to that expected from ocean outgasing without any additional contribution from tropical deforestation.

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