

# CHAPTER 1

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## Long-Lived Ozone-Related Compounds

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# CHAPTER 1

## LONG-LIVED OZONE-RELATED COMPOUNDS

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## SCIENTIFIC SUMMARY

Since the previous Assessment (WMO, 1995), significant progress has been achieved in determining and understanding the distributions of long-lived ozone-related gases in both the troposphere and stratosphere. In this chapter, we deal primarily with long-lived halocarbons (chlorofluorocarbons (CFCs), halons, perfluorinated and perchlorinated compounds) and other significant long-lived non-halocarbon species.

- Tropospheric measurements show that:
  - (a) International “compliance” with the Montreal Protocol and its Amendments has resulted in the amounts of most CFCs and chlorocarbons in the atmosphere being equal to or lower than amounts that are consistent with the Protocol’s provisions regarding production and emission.
  - (b) The total amount of organic chlorine ( $\text{CCl}_y$ ) contained in long- and short-lived chlorocarbons reached maximum values of  $3.7 \pm 0.1$  parts per billion (ppb) between mid-1992 and mid-1994 and is beginning to decrease slowly in the global troposphere. This slowing down and reversal in the growth rate resulted primarily from reduced emissions of methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ).
  - (c) Despite significant reduction in the emission of halons, the total amount of organic bromine in the troposphere continues to rise, largely because of the ongoing growth of Halon-1211 ( $\text{CBrClF}_2$ ). Possible causes are releases during the 1990s from the large halon “bank” that accumulated in developed countries during the 1980s and from increased production of Halon-1211 in developing countries. The recent observations of Halon-1211 concentrations are higher and growing faster than concentrations calculated from emissions derived from industry and United Nations Environment Programme (UNEP) data. Halon increases over the next few years could delay the time of the currently expected total organic bromine maximum in the troposphere.
  - (d) The amount of nitrous oxide ( $\text{N}_2\text{O}$ ) in the troposphere continues to increase at 0.2 to 0.3% per year. As concluded in previous assessments, this trend indicates that the global sources exceed the sinks by approximately 30%. The imbalance appears to be caused by anthropogenic sources whose relative strengths remain uncertain.
- Stratospheric measurements reflect the tropospheric chlorocarbon changes with a time delay ranging from 3 to 6 years, depending on latitude and altitude. Assuming the maximum delay, the peak in chlorine loading in the middle stratosphere (and consequently chlorine-catalyzed ozone loss) is expected to be reached around the year 2000. The impact of organic bromine is not going to significantly alter the time of maximum ozone depletion.

Specifically:

- (a) Space-based measurements of hydrogen chloride (HCl) near the stratopause and of total chlorine throughout the stratosphere are consistent with the amount and rate of change of total  $\text{CCl}_y$  in the troposphere. The rate of increase of stratospheric chlorine has slowed in recent years.
- (b) The rate of increase of the total amount of inorganic chlorine ( $\text{Cl}_y$ ) in the atmosphere obtained by combining HCl and chlorine nitrate ( $\text{ClONO}_2$ ) ground-based measurements and a model-computed chlorine monoxide (ClO) background has slowed significantly, from about 3.7% per year in 1991 to 1992 to about 1.8% per year in 1995 to 1996.

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- (c) The long-term remote monitoring of hydrogen fluoride (HF) near 55 km altitude from space and of total column amounts of HF and carbonyl fluoride (COF<sub>2</sub>) from the ground, along with the HCl trends, have confirmed that CFC and chlorocarbon compounds included in the Montreal Protocol have been the principal sources of both inorganic fluorine and Cl<sub>y</sub> in the stratosphere.
- (d) Volcanoes have not contributed significantly in recent decades to the total amount of chlorine in the stratosphere.
- Industrial production, sales data, and end-use modeling indicate that global emissions of the long-lived CFCs (-11, -12, -113, -114, and -115), carbon tetrachloride (CCl<sub>4</sub>), and Halon-1211 and -1301 (CBrF<sub>3</sub>) are all in decline. For CFC-12 (CCl<sub>2</sub>F<sub>2</sub>) and Halon-1211, the emissions still exceed their atmospheric removal rates; hence, their concentrations are still increasing.
- Estimations using global tropospheric measurements and atmospheric chemical models show that:
  - (a) The CFCs whose emissions are accurately known appear to have atmospheric lifetimes consistent with destruction in the stratosphere being their principal removal mechanism.
  - (b) CFC and chlorocarbon emissions inferred from atmospheric observations are consistent, approximately, with independent estimates of emissions based on industrial production and sales data. CFC-113 (CCl<sub>2</sub>FCClF<sub>2</sub>) is an exception: emissions based on atmospheric observations are significantly lower than those calculated by industry.
  - (c) While CCl<sub>4</sub> in the atmosphere is declining at approximately 0.8% per year, the interhemispheric difference is effectively constant, indicating that there are still significant Northern Hemispheric (NH) emissions. Atmospheric measurements and estimates of developed countries' emissions indicate that developing countries have dominated world releases of CCl<sub>4</sub> after 1991. A recent investigation of stratospheric CCl<sub>4</sub> observations and some three-dimensional (3-D) model studies suggest that its lifetime is closer to 35 years, instead of the previously reported 42 years; if this shorter lifetime is correct, then larger emissions are indicated, presumably from developing countries.
  - (d) Perfluorocarbons (PFCs) and sulfur hexafluoride (SF<sub>6</sub>) continue to increase in the background atmosphere. They are not ozone depleters but are of potential concern because they are strong absorbers of infrared radiation on a per-molecule basis and, once released, they persist in the atmosphere for millennia.
- Simultaneous determinations of the stratospheric mixing ratio of a species and the age of the air can be used together with tropospheric measurements to estimate steady-state atmospheric lifetimes for species that lack tropospheric sinks. In general, the lifetimes obtained in this way are consistent with the model-derived lifetime ranges and lifetimes based on tropospheric measurements. However, the recommended reference lifetimes for CFC-11 (CCl<sub>3</sub>F) and CCl<sub>4</sub> are approximately 45 and 35 years, respectively, which are shorter than the previously recommended estimates (50 and 42 years, respectively); some recent 3-D models also support these changes. Recommended reference lifetimes for major ozone-depleting source gases discussed in this chapter and also in Chapter 2 are summarized in Table 1-1.

**Table 1-1. Summary of current (WMO, 1998) and previous (WMO, 1995) reference and observed steady-state lifetimes for several ozone-related source species.** Lifetime is defined as the total amount of a compound in the atmosphere divided either by its total rate of removal or by its rate of destruction by tropospheric OH alone (values in parentheses). Additional information on calculated ranges for different models and lifetime-related uncertainties can be found in Tables 1-3, 1-4, 1-5, 1-6, and in Chapter 2 (Tables 2-2, 2-4, and 2-6).

Industrial Name	Chemical Formula	Lifetime, WMO (1998) <sup>a</sup> (years)	Lifetime, Observed Range (years)	Lifetime, WMO (1995) (years)
Nitrous oxide	N <sub>2</sub> O	120	75 to 173 <sup>d</sup>	120
CFC-11	CCl <sub>3</sub> F	45 <sup>f</sup>	29 to 76 <sup>e</sup>	50
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	100	77 to 185 <sup>e</sup>	102
CFC-113	CCl <sub>2</sub> FCClF <sub>2</sub>	85	54 to 143 <sup>d</sup>	85
Carbon tetrachloride	CCl <sub>4</sub>	35 <sup>f</sup>	21 to 43 <sup>d</sup>	42
H-1211	CBrClF <sub>2</sub>	11 <sup>f</sup>	10 to 31 <sup>d</sup>	20
H-1301	CBrF <sub>3</sub>	65	60 to 65 <sup>g</sup>	65
Methyl chloroform	CH <sub>3</sub> CCl <sub>3</sub>	4.8 (5.7)	4.5 to 5.1 <sup>b</sup>	5.4
HCFC-22	CHClF <sub>2</sub>	11.8 (12.3)	7.0 to 14.4 <sup>c</sup>	13.3
HCFC-141b	CH <sub>3</sub> CCl <sub>2</sub> F	9.2 (10.4)	(h)	9.4
HCFC-142b	CH <sub>3</sub> CClF <sub>2</sub>	18.5 (19.5)	(h)	19.5
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	13.6 (14.1)	(h)	14
HFC-23	CHF <sub>3</sub>	243 (255)	(h)	250
Methyl chloride	CH <sub>3</sub> Cl	~1.3 (1.3)	(h)	1.5
Methyl bromide	CH <sub>3</sub> Br	0.7 (1.8)	(h)	1.3
Methane	CH <sub>4</sub>	8.9 <sup>i</sup> (9.3)	(h)	10

<sup>a</sup> The numbers in parentheses represent lifetimes for removal by tropospheric OH scaled to the total atmospheric lifetime of CH<sub>3</sub>CCl<sub>3</sub> (4.8 years) derived by Prinn *et al.* (1995), and adopting CH<sub>3</sub>CCl<sub>3</sub> lifetimes for ocean removal of 85 years and stratospheric removal of 45 years (Kaye *et al.*, 1994). Adopting a shorter stratospheric removal time of 37 years (Prinn *et al.*, 1995; see also Volk *et al.*, 1997) yields a lifetime for CH<sub>3</sub>CCl<sub>3</sub> removal by tropospheric OH of 5.9 years which is within the uncertainty limits of the above (WMO, 1998) reference value.

<sup>b</sup> Prinn *et al.*, 1995.

<sup>c</sup> Miller *et al.*, 1998.

<sup>d</sup> Volk *et al.*, 1997. Note that this analysis gives only stratospheric lifetimes. Additional loss of H-1211 in the troposphere (see Section 1.4.4) reduces its lifetime to 11 years. When considering recently updated emissions of H-1211 (see Figure 1-11) and observations, the Butler *et al.* (1998) lifetime evaluation approach leads to an H-1211 lifetime of 10 years.

<sup>e</sup> For CFC-11, combined range of Volk *et al.* (1997) and updated values from Cunnold *et al.* (1997); for CFC-12, range covered by the central estimates of Volk *et al.* (1997) and updated central estimates from Cunnold *et al.* (1997).

<sup>f</sup> WMO 1998 CFC-11, H-1211, and CCl<sub>4</sub> lifetimes are lower than WMO (1995) values to take account of recent estimates based on stratospheric observations and models. Note that some calculations in later chapters were carried out before these WMO (1998) values were finalized and therefore used WMO (1995) values instead.

<sup>g</sup> Butler *et al.*, 1998.

<sup>h</sup> Not available or not applicable.

<sup>i</sup> Lifetime as calculated by Prinn *et al.* (1995). The adjustment time for CH<sub>4</sub> recovery would be somewhat longer due to CH<sub>4</sub> feedback on CO and OH (WMO, 1995).

## 1.1 INTRODUCTION

A wide range of long- and short-lived trace gases play very significant roles in the atmosphere. These roles include production of nitrogen, chlorine, bromine, and hydrogen free radicals that control catalytic ozone destruction in the stratosphere, and perturbations of the atmospheric infrared (IR) radiative budget that can force climatic change.

These gases are conveniently divided into two classes depending on whether their atmospheric chemical destruction occurs predominantly (or exclusively) in the stratosphere, or predominantly in the troposphere; the former are generally longer-lived than the latter. In this chapter, we focus primarily on those long-lived gases for which stratospheric processes govern their chemical removal. In Chapter 2, gases with major tropospheric sinks (including reaction with hydroxyl free radicals) are discussed. We emphasize, however, that these two classes of gases share many common factors in both their life cycles and effects. Hence these two chapters are closely linked and not merely complementary.

The number of measurements of the atmospheric concentrations of long-lived gases has increased significantly since the previous Assessment (WMO, 1995), at which time a complementary comprehensive review of measurements and lifetimes of the halogenated source gases was also produced (Kaye *et al.*, 1994). Since then, important new remote sensing and in situ sampling datasets have been obtained. In addition to the continuation of ground-based sampling by global networks of stations around the globe that have provided measurements of the temporal evolution of gases in the troposphere, there have been ground-, aircraft-, balloon-, and space-based instruments that have provided complementary views of the total column abundances and vertical distributions of the gaseous sources and sinks of ozone-depleting catalysts on a near-global scale.

Substantial progress in the understanding of the precision and accuracy of measurement techniques has recently resulted from the implementation of intercomparison and independent absolute calibration activities to achieve better accuracy and internal and long-term consistency among a number of databases reported on or referred to in this chapter. A successful example of such activities is the independent development of calibrations in the two major ground-based in situ networks, Advanced Global Atmospheric

Gases Experiment (AGAGE) (Prinn *et al.*, 1998) and National Oceanic and Atmospheric Administration-Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) (Elkins *et al.*, 1998), and the intercomparisons of these and other calibrations in the Nitrous Oxide and Halocarbons Intercomparison Experiment (NOHALICE) (Fraser *et al.*, 1996; Oram *et al.*, 1996; Cunnold *et al.*, 1997; Miller *et al.*, 1998). The general aim of NOHALICE is to compare the trace gas standards (for nitrous oxide (N<sub>2</sub>O), chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), halons, perfluorocarbons (PFCs), and other halocarbon species) used in various laboratories around the world making long-term, background measurements of these chemicals. This activity enables datasets for individual species obtained from participating laboratories to be ultimately combined, on a common calibration scale, for subsequent analysis and interpretation. Typical performances achieved within NOHALICE are provided in Section 1.2.1.

Important developments for the upper atmosphere include the Network for the Detection of Stratospheric Change (NDSC), which is a ground-based, long-term, international measuring network specifically designed to make worldwide observations through which changes in the physical and chemical state of the stratosphere can be determined and understood (Kurylo and Solomon, 1990). This dual objective requires high-precision, state-of-the-art measurements of ozone as well as a broad range of chemical species and dynamical tracers that influence ozone chemistry. These measurement requirements have been achieved by properly selecting a suite of primary NDSC instruments (lidars, ultraviolet (UV)-visible spectrometers, Fourier transform infrared (FTIR) instruments, microwave radiometers, balloon sondes, etc.) and establishing documented procedures for instrument- and retrieval algorithm intercomparisons, as well as protocols for archiving "NDSC-quality" data (for additional information, visit the World Wide Web site <http://climon.wwb.noaa.gov>).

A large amount of information on the vertical distribution of atmospheric compounds has been further acquired since the 1994 Assessment (WMO, 1995) during airplane- and balloon-campaigns, as well as space-based missions, among which the Upper Atmospheric Research Satellite (UARS) (Reber *et al.*, 1993) and the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment (Kaye and Miller, 1996; Gunson *et al.*, 1996) have provided substantial data of relevance to this

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chapter. Assessments of space-based data using nearly coincident measurements with airplane- and balloon-based instruments have contributed to measurement quality control and estimation of accuracy; relevant examples are described later in this chapter.

In the following three sections of this chapter we address primarily the current status of the concentrations, long-term trends, and global halogen loading budgets of halogens based on measurements performed since the 1994 Assessment and, finally, we summarize the recent findings about atmospheric lifetimes for a number of them.

Concentrations of long-lived gases and their trends are discussed for five subclasses, namely, CFCs, chlorobromocarbons including halons, fluorinated compounds ( $\text{SF}_6$ ,  $\text{CF}_4$ , etc.), perchlorinated compounds ( $\text{CCl}_4$ ), and significant miscellaneous species ( $\text{N}_2\text{O}$ , HF, HCl, etc.). In each case, measured behavior in both the troposphere and stratosphere are addressed. Also reviewed is information on the preindustrial abundances of these compounds where available and relevant. The contributions of this ensemble of chemicals to the global budgets of chlorine, bromine, and fluorine are fundamental to quantification of the magnitude and trend of ozone depletion induced by them. These budgets can be elucidated by judicious use of tropospheric and stratospheric observations, reported emissions from industrial and other anthropogenic activity, and fitting of model simulations to observations (by trial and error or preferably optimally).

Deduction of the atmospheric lifetime, defined as the atmospheric content divided by the atmospheric removal rate of the gas, is fundamental to testing chemical theory and to ranking the contributions of each gas to ozone depletion. We discuss lifetime determinations based on three complementary approaches: modeling using laboratory measurements of rate constants and absorption cross sections, estimates using stratospheric and tropospheric measurements, and inverse methods, which optimally fit model simulations to tropospheric measurements. The last approach uses industrial estimates of emissions.

In this chapter, we further seek answers to several key scientific questions. Are observed trends for various gases consistent with expectations based on reported emissions, and are the latter complying with the Montreal Protocol? Has the total atmospheric chlorine and bromine contained in these chemicals peaked? Are tropospheric and stratospheric trends consistent? Are measured concentrations and temporal variations

consistent with estimates of industrial emissions and chemical theory? Finally, what are the lifetimes of these gases and what are the major sources of uncertainty in their estimation?

Ground-based stations cited in the chapter, along with their geographic coordinates, are listed in the Appendix of this chapter. Unless otherwise stated, the terms “concentrations,” “abundances,” “loadings,” “mixing ratios,” and “volume mixing ratios” refer to concentrations as dry air mole fractions. Acronyms and all species, generally referred to by their chemical formulae, are defined in the appendices of this Assessment report.

## 1.2 CONCENTRATION MEASUREMENTS AND TRENDS

This section updates the review of abundances and trends of CFCs, halons, carbon tetrachloride ( $\text{CCl}_4$ ), PFCs,  $\text{SF}_6$ ,  $\text{N}_2\text{O}$ , and other relevant species compiled by Sanhueza *et al.* (1995) in WMO (1995). Table 1-2 lists the 1992, 1995, and 1996 concentrations and recent growth rates for these long-lived trace gases, as well as for the species from Chapter 2, that make significant contributions to tropospheric budgets of chlorine, bromine, and fluorine.

### 1.2.1 Data Calibration and Intercomparisons

During the past decade, a variety of measurement techniques has been used in various programs to assess the current and past chemical composition of the atmosphere. This has required independent calibration and intercomparison activities to improve absolute accuracy and achieve long-term consistency amongst the respective datasets.

Air samples, collected at clean-air sites, have been used to compare absolute calibrations of  $\text{N}_2\text{O}$  and halocarbon measurements made at a number of international laboratories since the late 1970s (Rasmussen, 1978; Fraser, 1980). Such activities have been expanded significantly by the establishment of the Nitrous Oxide and Halocarbons Intercomparison Experiment (NOHALICE), an International Global Atmospheric Chemistry (IGAC) Project activity. Two types of intercomparison experiments have been conducted within the NOHALICE framework. The first involves the circulation of a common background air sample among participating laboratories for trace gas

**Table 1-2. Global tropospheric concentrations and trends for CFCs, halons, chlorocarbons, HCFCs, HFCs, PFCs, SF<sub>6</sub>, and N<sub>2</sub>O.** The 1992 data from the previous (1994) Assessment (Sanhueza *et al.*, 1995) are shown in parentheses. The 1992 data not in parentheses are from this current Assessment. Note the large change in the CCl<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub> concentrations for 1992, due to the adoption of new calibration scales in AGAGE (CH<sub>3</sub>CCl<sub>3</sub>, Prinn *et al.*, 1995; CCl<sub>4</sub>, Simmonds *et al.*, 1998) and smaller changes in the NOAA/CMDL calibration scales for CCl<sub>2</sub>F<sub>2</sub> and CCl<sub>4</sub> (Elkins *et al.*, 1998). The growth rates are the average increase over the period 1995-1996 or from the most recent available data. The relevant references are given in the text.

Species	Industrial Name	Concentration (ppt)			Growth		Laboratory <sup>d</sup>	Method
		1992	1995	1996	ppt yr <sup>-1</sup>	% yr <sup>-1</sup>		
<b>CFCs</b>								
CCl <sub>2</sub> F <sub>2</sub>	CFC-12	(503) 504	524.6	529.7	5.1±0.5	1.0	AGAGE	in situ
		505	526.7	530.4	3.7±0.2	0.7	NOAA/CMDL	in situ
CCl <sub>3</sub> F	CFC-11	(268) 263	264.3	263.6	-0.7±0.3	-0.3	AGAGE	in situ
		271	271.4	270.7	-0.7±0.2	-0.3	NOAA/CMDL	in situ
CClF <sub>3</sub>	CFC-13	4			0.2	5	MPAE	flask, NH
CCl <sub>2</sub> FCClF <sub>2</sub>	CFC-113	(82) 80	83.0	83.0	0.0±0.2	0.0	AGAGE	in situ
		81	84.0	84.0	0.1±0.1	0.1	NOAA/CMDL	flask
CClF <sub>2</sub> CClF <sub>2</sub>	CFC-114	(20) 15			1.2	8	MPAE, UCI, UT	flask, NH
CClF <sub>2</sub> CF <sub>3</sub>	CFC-115	5			0.4	8	MPAE, NCAR	flask, NH
<b>Halons</b>								
CBrClF <sub>2</sub>	H-1211	(2.5) 2.7	3.22	3.40	0.18±0.03	5.4	NOAA/CMDL	flask
		2.9	3.55	3.82	0.27±0.02	7.3	UEA	flask, SH
CBrF <sub>3</sub>	H-1301	(2.0) 1.9	2.27	2.29	0.02±0.03	0.9	NOAA/CMDL	flask
		1.7	1.96	2.02	0.06±0.04	3.0	UEA	flask, SH
CBr <sub>2</sub> F <sub>2</sub>	H-1202	0.02	0.031	0.037	0.006±0.001	18	UEA	flask, SH
CBrF <sub>2</sub> CBrF <sub>2</sub>	H-2402		0.47	0.48	0.01±0.01	1.9	NOAA/CMDL	flask
		0.36	0.41	0.42	0.01±0.01	2.4	UEA	flask, SH
<b>Chlorocarbons</b>								
CH <sub>3</sub> Cl		(600)		550			Chapter 2	
CCl <sub>4</sub>		(132) 103	100.8	99.7	-1.1±0.3	-1.1	AGAGE	in situ
		106	104.1	103.2	-0.9±0.1	-0.9	NOAA/CMDL	in situ
CH <sub>3</sub> CCl <sub>3</sub>		(160) 127	102.5	88.7	-13.2	-14	AGAGE	in situ
			110	97	-14	-14	NOAA/CMDL	in situ
COCl <sub>2</sub>				20			Chapter 2	
<b>Bromocarbons<sup>a</sup></b>								
CH <sub>3</sub> Br		(11)		9-11			Chapter 2	
CH <sub>2</sub> Br <sub>2</sub>				0.6-1.0			Chapter 2	
CHBr <sub>3</sub>				0.2-0.6			Chapter 2	
CH <sub>2</sub> BrCl				0.1-0.2			Chapter 2	
CHBrCl <sub>2</sub>				0.1-0.2			Chapter 2	
CHBr <sub>2</sub> Cl				0.1			Chapter 2	
CH <sub>2</sub> BrCH <sub>2</sub> Br				0.1			Chapter 2	

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Table 1-2, continued.

Species	Industrial Name	Concentration (ppt)			Growth		Laboratory <sup>d</sup>	Method
		1992	1995	1996	ppt yr <sup>-1</sup>	% yr <sup>-1</sup>		
<b>HCFCs</b>								
CHClF <sub>2</sub>	HCFC-22 (102)	102	117	122	5.0	4.2	NOAA/CMDL	flask
			119	125	5.7	4.5	AGAGE	flask
CH <sub>3</sub> CCl <sub>2</sub> F	HCFC-141b	(0.3)	3.5	5.4	1.9	43	NOAA/CMDL	flask
		0.13					UEA	flask, SH
CH <sub>3</sub> CClF <sub>2</sub>	HCFC-142b	(3.5)	3.1	6.6	1.1	15	NOAA/CMDL	flask
		1.9		7.6			UEA	flask, SH
<b>HFCs</b>								
CHF <sub>3</sub>	HFC-23	9.0	10.7		0.55	5.1	UEA	flask, SH
CH <sub>2</sub> FCF <sub>3</sub>	HFC-134a		1.6	3.0	1.4	59	NOAA/CMDL	flask
		0.03	0.7		0.64	91	UEA	flask, SH
<b>PFCs</b>								
CF <sub>4</sub>	PFC-14	(70) 72	75		1.00±0.05	1.3	MPAE	flask, NH
			74		1.1±0.4	1.5	ATMOS	FTIR, NH
CF <sub>3</sub> CF <sub>3</sub>	PFC-116	(4) 2.4	2.6		0.084±0.005	3.2	MPAE	flask, NH
<b>Others</b>								
SF <sub>6</sub>			3.5	3.7	0.24±0.01	6.9	NOAA/CMDL	flask
		(2-3) 2.7	3.4	3.7	0.27	7.2	UH	flask
			4.0	4.2	0.2	4.8	ULg	FTIR, NH
N <sub>2</sub> O <sup>b</sup>	(310)	308	310.0	311.1	1.0±0.3	0.3	AGAGE	in situ
		309.9	311.6	312.4	0.8±0.3	0.3	NOAA/CMDL	in situ
Total Cl <sup>c</sup>				3580	-25	-0.7		
Br				20.2	0.23	1.1		
F				2370	44	1.8		

<sup>a</sup> For most bromocarbon concentrations listed, refer to Table 2-7 to assess local variability.

<sup>b</sup> N<sub>2</sub>O concentrations and growth rates are in parts per billion (ppb) and ppb yr<sup>-1</sup>.

<sup>c</sup> Add about 100 ppt for source species not considered here (e.g., CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>2</sub>CCl<sub>2</sub>, etc.) discussed in Chapter 2.

<sup>d</sup> Advanced Global Atmospheric Gases Experiment (AGAGE); Atmospheric Trace Molecule Spectroscopy (ATMOS); Max-Planck-Institute for Aeronomy (MPAE); National Center for Atmospheric Research (NCAR); National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL); University of California at Irvine (UCI); University of East Anglia (UEA); University of Heidelberg (UH); University of Liège (ULg); University of Tokyo (UT); Chapter 2 entries refer to Chapter 2 of the current Assessment (WMO, 1998).

analyses, thus achieving a direct comparison, via the same air sample, between these laboratories. The second involves sending air samples from the same clean air location, collected at the same time or close together, to various laboratories for trace gas analyses. The resulting data are compared, thus achieving an indirect comparison between laboratories. Laboratories that have participated in one or both types of NOHALICE intercomparisons are from Australia (Commonwealth Scientific and

Industrial Research Organisation (CSIRO)), Germany (University of Heidelberg), Japan (University of Tokyo), South Africa (Department of Scientific and Industrial Research (DSIR)), United Kingdom (University of Bristol, University of East Anglia (UEA)) and United States (National Center for Atmospheric Research (NCAR), NOAA/CMDL, Oregon Graduate Institute (OGI), University of California at Irvine (UCI), Scripps Institution of Oceanography (SIO)-AGAGE, and United

States Geological Survey (USGS)). Species that have been compared by one or both intercomparison methods include N<sub>2</sub>O; CFC-11, -12, and -113 (CCl<sub>3</sub>F, CCl<sub>2</sub>F<sub>2</sub>, and CCl<sub>2</sub>FCClF<sub>2</sub>); HCFC-22, -141b, and -142b (CHClF<sub>2</sub>, CH<sub>3</sub>CCl<sub>2</sub>F, CH<sub>3</sub>CClF<sub>2</sub>); HFC-134a (CH<sub>2</sub>FCF<sub>3</sub>); Halon-1211, -1301, and -2402 (CBrClF<sub>2</sub>, CBrF<sub>3</sub>, and CBrF<sub>2</sub>CBrF<sub>2</sub>); methyl chloroform (CH<sub>3</sub>CCl<sub>3</sub>); CCl<sub>4</sub>; methyl chloride (CH<sub>3</sub>Cl); methyl bromide (CH<sub>3</sub>Br); and SF<sub>6</sub>.

Comparisons have been published for CCl<sub>2</sub>FCClF<sub>2</sub> (NOAA/CMDL, OGI, SIO-AGAGE, U. Tokyo); CH<sub>3</sub>CCl<sub>2</sub>F, CH<sub>3</sub>CClF<sub>2</sub>, and CH<sub>2</sub>FCF<sub>3</sub> (NOAA/CMDL, UEA); CHClF<sub>2</sub> (NOAA/CMDL, SIO-AGAGE); CBrClF<sub>2</sub>, CBrF<sub>3</sub>, and CBrF<sub>2</sub>CBrF<sub>2</sub> (NOAA/CMDL, UEA). A summary of the comparability between participating laboratories in NOHALICE for various species is shown in Table 1-3.

Most routine measurements of the stratospheric distribution of CFCs and other long-lived species have been performed by whole air sampling with subsequent gas chromatographic analysis (e.g., Kaye *et al.*, 1994). More recently, however, in situ measurements using automated gas chromatographic methods have become available for both aircraft (e.g., the Airborne Chromatograph for Atmospheric Trace Species-IV (ACATS-IV) (Elkins *et al.*, 1996b; Bujok *et al.*, 1998)) and balloonborne platforms (e.g., the Lightweight Airborne Chromatograph Experiment (LACE) (F.L. Moore, NOAA/CMDL, U.S., personal communication, 1998)) that are able to measure with time resolutions of one to a few minutes, depending on the target gas. These instruments provide a much larger dataset than that obtained with whole air samplers (WAS) and avoid sample degradation. Intercomparisons between these

diverse techniques and measurements have resulted in a better understanding of calibration issues and improvements in accuracy (e.g., Chang *et al.*, 1996a,b; Sen *et al.*, 1998).

Remote sensing investigations, which derive atmospheric composition information from spectral absorption or emission features, rely upon spectroscopic parameters determined in the laboratory to invert these features into concentrations. The uncertainty of the reported concentrations reflects the accuracy with which these spectroscopic parameters have been obtained. The most recently updated line parameters compilation has been described by Rothman *et al.* (1998), and Abrams *et al.* (1996a) have evaluated the precision and accuracy with which concentrations of some 30 key atmospheric constituents can be derived from IR space-based solar occultation observations.

Two space-based experiments have provided substantial data for this chapter, namely the Halogen Occultation Experiment (HALOE) on the UARS satellite (Russell *et al.*, 1993) and Atmospheric Trace Molecule Spectroscopy (ATMOS) on shuttles (Gunson *et al.*, 1996). Besides having their individual datasets intercompared, these experiments were involved in intercomparison and validation tests based on independent measurements provided by ground-, airplane-, and balloon-based instruments (a description of the evaluation of the UARS data has been reported in a special issue of *Journal of Geophysical Research*, Vol. 101, No. D6, pp. 9539-10476, 1996). On that basis, Russell *et al.* (1996a,b) reported intercomparison exercises indicating that HALOE concentration measurements of HCl and HF throughout the middle atmosphere could be retrieved with an accuracy of 5 to

**Table 1-3. The differences between participating laboratories in NOHALICE for measurements of N<sub>2</sub>O and various halocarbon species.** The number of participating laboratories is given in parentheses after each species (Oram *et al.*, 1995, 1996; Fraser *et al.*, 1996, 1998; Miller *et al.*, 1998; Geller *et al.*, 1997; P. Fraser, CSIRO, Australia, personal communication of unpublished NOHALICE data, 1998).

Species	Differences (%) between laboratories
N <sub>2</sub> O (3), CCl <sub>2</sub> F <sub>2</sub> (4), CHClF <sub>2</sub> (2), CH <sub>3</sub> Cl (2), SF <sub>6</sub> (2)	≤ 1
CCl <sub>2</sub> FCClF <sub>2</sub> (4), CCl <sub>4</sub> (3), CH <sub>3</sub> CCl <sub>2</sub> F (2)	3 to 6
CCl <sub>3</sub> F (4), CBrClF <sub>2</sub> (2), CBrF <sub>3</sub> (2), CBrF <sub>2</sub> CBrF <sub>2</sub> (2), CH <sub>3</sub> Br (2)	8 to 10
CH <sub>3</sub> CCl <sub>3</sub> (3), CH <sub>3</sub> CClF <sub>2</sub> (2), CH <sub>2</sub> FCF <sub>3</sub> (2)	20 to 35

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10%. ATMOS was a core part of the 1992, 1993, and 1994 Space Shuttle-based Atmospheric Laboratory for Applications and Science (ATLAS) missions (Kaye and Miller, 1996). Assessments were made of absolute accuracy and efficiency of retrieval methods, based on simultaneous measurements of identical parameters and on intercomparisons of collocated measurements by UARS experiments, including HALOE and the Cryogenic Limb Array Etalon Spectrometer (CLAES) (Nightingale *et al.*, 1996). During the 1994 ATLAS-3 mission, a series of ATMOS measurements were near-coincident with a flight of the NASA ER-2 high-altitude aircraft at northern midlatitudes as part of the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) campaign. The intercomparisons of volume mixing ratio profiles for a number of tracers of atmospheric transport (Chang *et al.*, 1996a) and halogenated gases (Chang *et al.*, 1996b) showed good agreement between the ER-2 in situ and ATMOS remote measurements, with the exception of  $\text{CCl}_4$  (15% differences) and carbon monoxide (CO) (up to 25% differences in the lower stratosphere).

To provide independent calibration and validation measurements for space-based measurements, the NDSC has established specific activities to ensure data quality. These include intercomparison campaigns among instruments that can be brought to a common site and, if this is not feasible, regular side-by-side exercises using portable instruments that travel to the various stations of the network are organized. Details on the NDSC composition, organization, and activities can be found on the worldwide web (<http://climon.wwb.noaa.gov>), while geophysical data verified according to the data quality protocols are archived at the NOAA/NDSC Data Center, Washington, D.C., U.S.

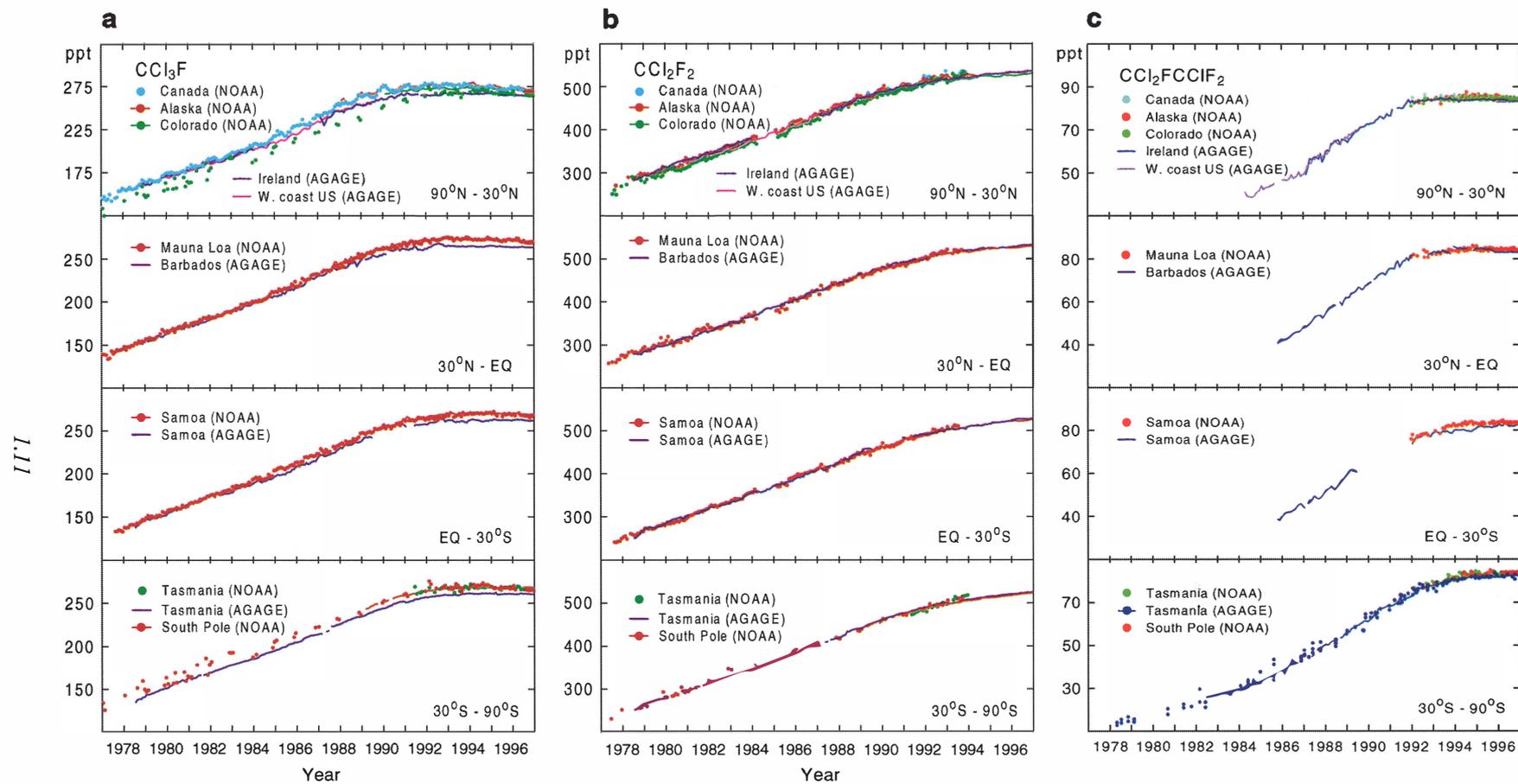
### 1.2.2 Chlorofluorocarbons (CFCs)

Figure 1-1 shows the  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CCl}_2\text{FCClF}_2$  mole fractions from the late 1970s through to the mid-1990s from surface sites of the ALE/GAGE/AGAGE (Prinn *et al.*, 1998) and NOAA/CMDL (Elkins *et al.*, 1998) networks. Tropospheric  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CCl}_2\text{FCClF}_2$  growth rates, as observed in the NOAA/CMDL global flask air sampling and in situ networks (Figure 1-1), have continued to decline. Global  $\text{CCl}_2\text{F}_2$  growth rates in 1995 to 1996 were approximately 4 parts per trillion (ppt)  $\text{yr}^{-1}$  (Table 1-2), having slowed down

by more than two-thirds since the late 1980s. For  $\text{CCl}_2\text{FCClF}_2$  and  $\text{CCl}_3\text{F}$ , tropospheric growth rates in 1995 to 1996 were near zero or in decline (0.1 and -0.7 ppt  $\text{yr}^{-1}$ , respectively) (Thompson *et al.*, 1994; Montzka *et al.*, 1996; Elkins *et al.*, 1996a, 1998).

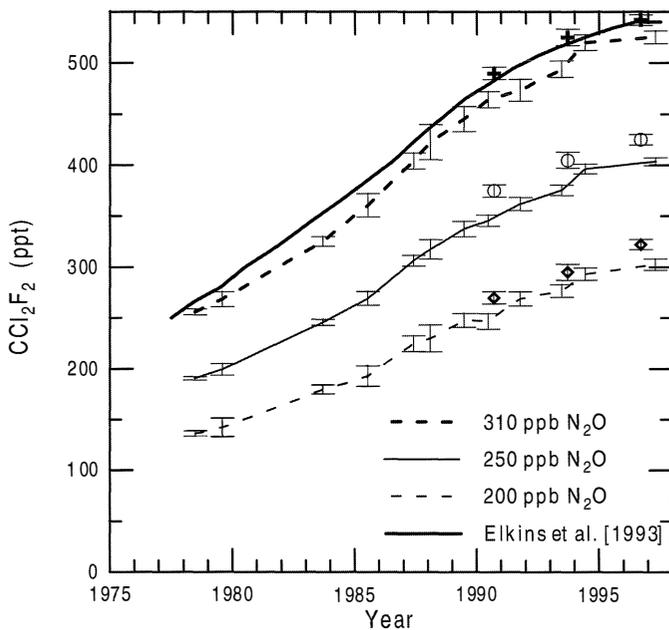
In situ observations from the Atmospheric Lifetime Experiment-Global Atmospheric Gases Experiment (ALE-GAGE)-AGAGE global network (Figure 1-1) showed that global levels of  $\text{CCl}_3\text{F}$  reached a maximum in 1993 (approximately 265 ppt) and started to decay in 1994, while  $\text{CCl}_2\text{F}_2$  continued to increase throughout the 1990s, but at growth rates clearly slowing down. These observations have been interpreted using a global two-dimensional (2-D) transport model and show that global emissions of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  since 1993 were lower than estimated by industry and have decreased faster than expected under the Montreal Protocol (Cunnold *et al.*, 1997; see also Figure 1-12).  $\text{CCl}_2\text{FCClF}_2$  abundances stopped growing by 1996 and remained static at about 83 ppt (Prinn *et al.*, 1998). The global release estimates by industry consistently exceed those deduced from atmospheric measurements by approximately 10% from 1980 to 1993. This difference suggests that up to 10% of past production of  $\text{CCl}_2\text{FCClF}_2$  might not yet have been released (Fraser *et al.*, 1996). The global mean in situ 1996 data (Table 1-2) for  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CCl}_2\text{FCClF}_2$  show AGAGE concentrations lower than NOAA/CMDL by 2.7, 0.1, and 1.2%, respectively.

Observations of  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CCl}_2\text{FCClF}_2$  in Japan and Antarctica by the University of Tokyo (UT) from flask air samples gave average 1996 concentrations of 266, 531, and 81 ppt, respectively (Makide *et al.*, 1987, 1994; Y. Makide, University of Tokyo, Japan, personal communication of unpublished data, 1998). The UT global data for CFCs agree to within 1 to 3% with AGAGE and NOAA/CMDL data from similar latitude sites (Table 1-2). The UT data show small, negative trends (1995-1996) for all three CFCs on Hokkaido (Japan), and small, positive trends in Antarctica, that are not inconsistent with the regional trends observed in the AGAGE and NOAA/CMDL global networks. The same laboratory (UT) reported an average 1992 CFC-114 ( $\text{CClF}_2\text{CClF}_2$ ) concentration and growth rate of 13.5 ppt and 0.6 ppt  $\text{yr}^{-1}$ , respectively (Chen *et al.*, 1994). The UCI global flask sampling program (Rowland *et al.*, 1994) gave average 1995 concentrations for  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CCl}_2\text{FCClF}_2$  of 266, 518, and 84 ppt, respectively (O.W. Wingenter, University of California



**Figure 1-1.** Monthly mean background data (in situ and flask) for  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CCl}_2\text{FCCIF}_2$  from the ALE/GAGE/AGAGE (Prinn *et al.*, 1998) and NOAA/CMDL (Elkins *et al.*, 1998) global networks.

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**Figure 1-2.** Temporal trend of  $\text{CCl}_2\text{F}_2$  (CFC-12) mole fraction derived from balloonborne whole air sampling for different  $\text{N}_2\text{O}$  levels of the stratosphere, i.e., 310 ppb  $\text{N}_2\text{O}$  (in the lowermost stratosphere), 250 ppb  $\text{N}_2\text{O}$  (about 19 km at midlatitudes) and 200 ppb  $\text{N}_2\text{O}$  (about 21.5 km) (Engel *et al.*, 1998). The values are corrected for an assumed tropospheric  $\text{N}_2\text{O}$  increase of about  $0.2\% \text{ yr}^{-1}$ . The crosses, circles, and diamonds indicate  $\text{CCl}_2\text{F}_2$  concentrations measured remotely with the MkIV FTIR balloon instrument (Sen *et al.*, 1996). The top solid black line refers to globally averaged tropospheric  $\text{CCl}_2\text{F}_2$  measurements from the NOAA/CMDL network (Elkins *et al.*, 1998).

at Irvine, United States, personal communication of unpublished data archived at UCI, 1998), in good agreement (within 2%) with the NOAA/CMDL and AGAGE data.

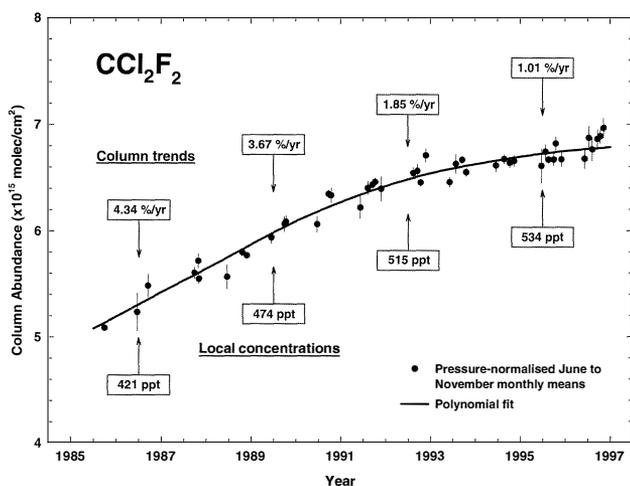
Extensive, aircraft-based air sampling campaigns were conducted in the NW Pacific (Pacific Exploratory Mission (PEM)-West A, September-October, 1991) and NE Atlantic (Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange (ASTEX/MAGE), June 1992) regions. Average free tropospheric values for  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CCl}_2\text{FCClF}_2$  of 274, 509, and 88 ppt, respectively (NW Pacific) and 267, 512, and 83 ppt, respectively (NE Atlantic) were obtained and a free tropospheric value of 15 ppt was observed for  $\text{CClF}_2\text{CClF}_2$  (Blake *et al.*, 1996a,b). Concentrations of  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_2\text{FCClF}_2$ , CFC-114 ( $\text{CClF}_2\text{CClF}_2$ ), and CFC-115 ( $\text{CClF}_2\text{CF}_3$ ) at the tropical tropopause in 1992 averaged 264, 494, 75, 16, and 4 ppt (Daniel *et al.*, 1996). A late 1980s/early 1990s Northern Hemisphere (NH) growth rate of  $0.4 \text{ ppt yr}^{-1}$  for  $\text{CClF}_2\text{CF}_3$  has been derived from NCAR data (Daniel *et al.*, 1996).

Tropospheric and stratospheric abundance data for several CFCs have been derived from balloonborne cryogenic air samplers flown at  $17.5^\circ\text{N}$ ,  $44^\circ\text{N}$ , and  $62^\circ\text{N}$  from 1977 to 1993 (Max-Planck-Institute for Aeronomy (MPAE), Germany) (Fabian *et al.*, 1996). Free troposphere abundances of  $\text{CClF}_3$ ,  $\text{CClF}_2\text{CClF}_2$ , and  $\text{CClF}_2\text{CF}_3$  (4, 15, and 5 ppt respectively) and growth rates

(5, 8, and  $8\% \text{ yr}^{-1}$  respectively) for 1990 have been derived from this dataset.

Vertical profiles of ozone-depleting substances (ODSs) extending into the stratosphere are important in assessing the relative contribution an individual ODS makes to total ozone depletion. Stratospheric measurements of ODSs up to 1990 were reviewed by Fraser *et al.* (1994). More recently, a large number of ODSs have been measured using whole air samples collected on balloon (Fabian *et al.*, 1994, 1996; Schmidt *et al.*, 1994; Lee *et al.*, 1995; Engel *et al.*, 1997, 1998; Patra *et al.*, 1997) and aircraft flights (Schaufler *et al.*, 1993; Woodbridge *et al.*, 1995; Daniel *et al.*, 1996). Stratospheric measurements of ODSs using in situ gas chromatography have been reported by Elkins *et al.* (1996b), Volk *et al.* (1997), and Wamsley *et al.* (1998). Sen *et al.* (1996) have reported mixing ratio profiles of  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_3\text{F}$ , and  $\text{CCl}_2\text{FCClF}_2$  from a balloon flight over New Mexico ( $34^\circ\text{N}$ ,  $104^\circ\text{W}$ ) during September 1993. The latter data provide mixing ratio profiles extending from 5 to 38 km, thus encompassing the entire free troposphere and most of the stratospheric layers of importance for these species.

Very few stratospheric datasets span a time frame that is sufficient for the investigation of stratospheric trends. The latter are different from those observed in the troposphere, due to the time lag associated with the exchange of air between the troposphere and the



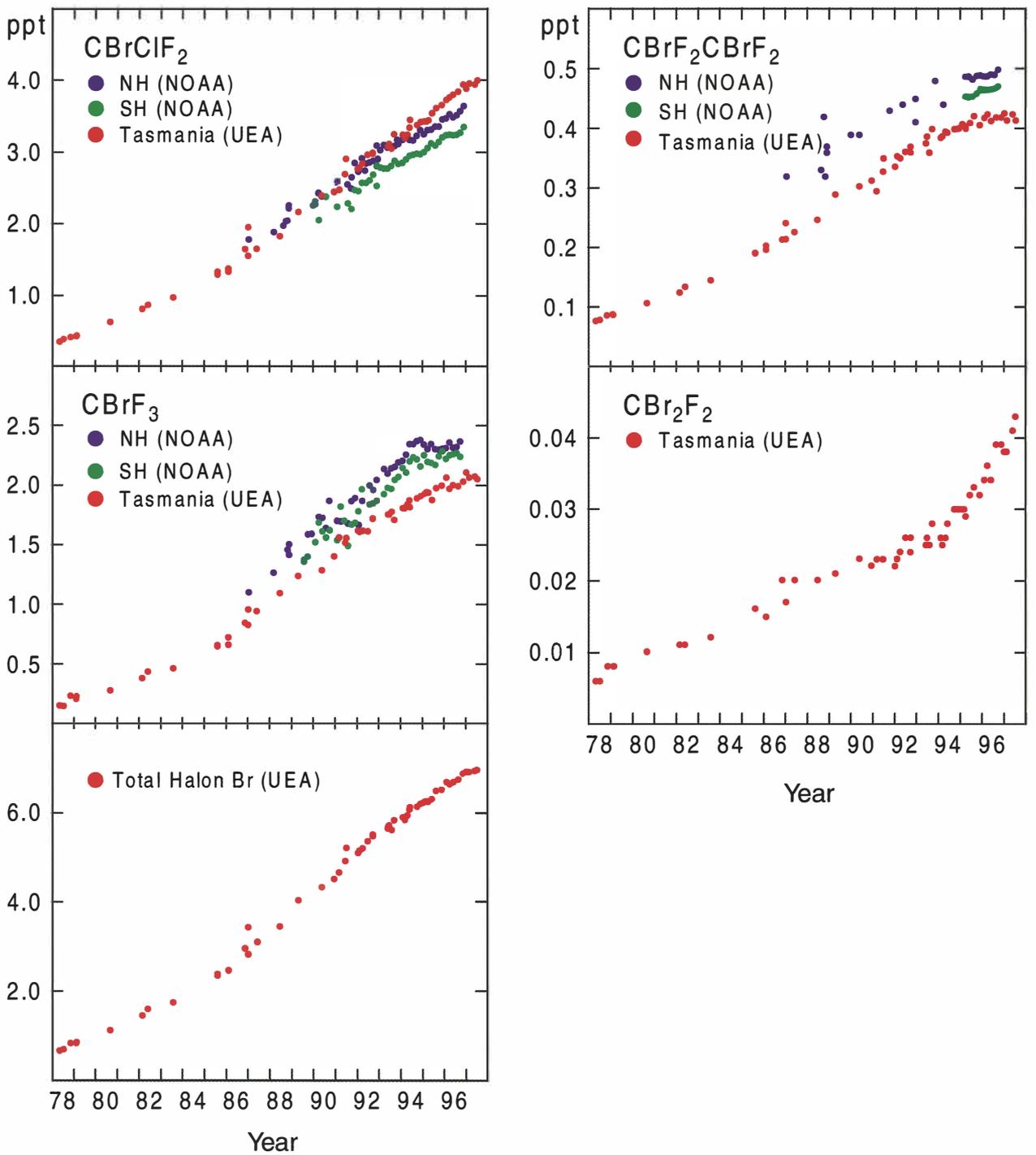
**Figure 1-3.** The evolution of the column amount of  $\text{CCl}_2\text{F}_2$  above the Jungfrauoch from 1985 to 1996, based on June to November monthly mean vertical column abundances. Column trends ( $\% \text{ yr}^{-1}$ ) and local volume mixing ratios (ppt) are indicated for 1986, 1989, 1992, and 1995 (Zander *et al.*, 1994a; updated with unpublished data). The continuous line is a 6<sup>th</sup> order polynomial fit to the data points.

stratosphere (the so-called “age” of stratospheric air; see Chapter 7) and due to the strong vertical gradients above the tropopause for many compounds that are destroyed in the stratosphere. These gradients differ with season and latitude and show significant short-term variations related to stratospheric dynamics, which can mask the long-term trends. One way of eliminating the short-term variations from the individual species data is to use another trace gas (e.g.,  $\text{N}_2\text{O}$ ) with similar behavior and no (or only a very small, well-defined) tropospheric increase as a reference substance. Based on this method, Engel *et al.* (1998) have derived stratospheric trends of  $\text{CCl}_2\text{F}_2$  (Figure 1-2) that are calibrated relative to the NOAA/CMDL standard. The small tropospheric trend of  $\text{N}_2\text{O}$  was taken into account by using 1993 as the base year with an approximately 310-ppb tropospheric mixing ratio for  $\text{N}_2\text{O}$ , and then assuming a trend of 0.2% forward and backward for all levels. In the lowermost stratosphere they reproduce the observed  $\text{CCl}_2\text{F}_2$  tropospheric trends quite well, with an average increase rate of  $18.5 \pm 1.8 \text{ ppt yr}^{-1}$  for the time period 1978 to 1990. At higher altitudes (i.e., lower  $\text{N}_2\text{O}$  levels) the absolute rates of increase were smaller due to photodissociation. For the time period from 1990 to 1997, a significant slowing down of the increase in the mixing ratio of  $\text{CCl}_2\text{F}_2$  was observed in the lowermost stratospheric level, with an increase rate of only  $11.9 \pm 4.2 \text{ ppt yr}^{-1}$ . Because of the larger difference in lifetime versus  $\text{N}_2\text{O}$ , this method gave less satisfactory results for  $\text{CCl}_3\text{F}$ , where a larger scatter in the correlations was observed. When compared with the global surface means from the NOAA/CMDL network (Elkins *et al.*, 1998), the differences in the observed  $\text{CCl}_2\text{F}_2$  stratospheric trend

(Figure 1-2) can be attributed to a time lag of about one year for tropospheric air to reach the lowermost stratosphere, in agreement with a time lag of about 0.8 years determined by Volk *et al.* (1997). The error bars represent the 1-sigma statistical uncertainty of the derived  $\text{CCl}_2\text{F}_2$  mixing ratio based on the fit between  $\text{N}_2\text{O}$  and  $\text{CCl}_2\text{F}_2$ . The sets of crosses, circles and diamonds in Figure 1-2 represent  $\text{CCl}_2\text{F}_2$  mixing ratios measured remotely by balloon at the 310, 250, and 200 ppb reference  $\text{N}_2\text{O}$  concentration levels on 27 September 1990, 25 September 1993, and 28 September 1996 (Sen *et al.*, 1996). While these data are biased high with respect to the in situ measurements (4 to 5%, which is commensurate with the accuracy of both techniques), they are in excellent agreement with the ground-based concentrations of  $\text{CCl}_2\text{F}_2$  displayed in Figure 1-1.

The total atmospheric loadings and long-term changes of various halogenated compounds can be determined by regular spectrometric observations from the ground. Figure 1-3 shows the evolution of the vertical column abundance of  $\text{CCl}_2\text{F}_2$  as retrieved from IR solar observations performed at the International Scientific Station of the Jungfrauoch (ISSJ, Switzerland) from the mid-1980s to 1996 (Zander *et al.* (1994a); R. Zander, University of Liège, Belgium, personal communication of unpublished data, 1998). The monthly mean  $\text{CCl}_2\text{F}_2$  column data (June to November only, to avoid significant variability during winter and spring) show rates of increase and local volume mixing ratios (assuming a standard distribution profile derived from in situ balloon soundings at northern midlatitudes) that compare very well with those displayed in Figure 1-1. The significant slowing down of the rate of increase of the  $\text{CCl}_2\text{F}_2$  column

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**Figure 1-4.** Measurements of CBrClF<sub>2</sub>, CBrF<sub>3</sub>, CBrF<sub>2</sub>CBrF<sub>2</sub>, CBr<sub>2</sub>F<sub>2</sub>, and total halon bromine made at UEA on air from the CSIRO Cape Grim air archive (SORG, 1996; Fraser *et al.*, 1998) and at NOAA/CMDL (CBrClF<sub>2</sub>, CBrF<sub>3</sub>, and CBrF<sub>2</sub>CBrF<sub>2</sub>) on air samples collected from their global flask sampling network (Montzka *et al.*, 1996; Butler *et al.*, 1998).

above ISSJ is a further manifestation of the reduction in the emissions of  $\text{CCl}_2\text{F}_2$  as imposed by the Montreal Protocol and its Amendments and Adjustments (see Figure 1-11).

### 1.2.3 Halons

The presence of bromine in the atmosphere has been given increased attention during recent years because of its high efficiency in destroying ozone and its continued atmospheric accumulation. The bromine-bearing source gases (halons) considered in this section are the long-lived  $\text{CBrClF}_2$ ,  $\text{CBrF}_3$ , and Halon-2402 ( $\text{CBrF}_2\text{CBrF}_2$ ), and the relatively short-lived Halon-1202 ( $\text{CBr}_2\text{F}_2$ ).

Throughout the 1990s, data from the NOAA/CMDL flask network showed that global abundances of  $\text{CBrClF}_2$  and  $\text{CBrF}_3$  continued to increase, with  $\text{CBrF}_3$  exhibiting a marked slowing in its growth rate in recent years (Thompson *et al.*, 1994; Montzka *et al.*, 1996; Elkins *et al.*, 1996a; Wamsley *et al.*, 1998). During 1996 the tropospheric abundances of  $\text{CBrClF}_2$ ,  $\text{CBrF}_3$ , and  $\text{CBrF}_2\text{CBrF}_2$  were 3.4, 2.3, and 0.48 ppt, respectively, with their 1995 to 1996 mole fractions growing at 0.18, 0.06, and 0.01 ppt yr<sup>-1</sup>, respectively (Figure 1-4; Butler *et al.*, 1998). Large amounts of  $\text{CBrF}_3$  and  $\text{CBrClF}_2$  are stored in fixed and portable fire fighting systems and emissions of these species could continue for decades, based on estimates of their current release rates (Butler *et al.*, 1998).

Measured tropospheric volume mixing ratios of  $\text{CBrClF}_2$ ,  $\text{CBrF}_3$ ,  $\text{CBrF}_2\text{CBrF}_2$ , and  $\text{CBr}_2\text{F}_2$  made at UEA on air from the CSIRO Cape Grim air archive (Langenfelds *et al.*, 1996) show large increases between 1978 and 1996. The 1996 concentrations for these species averaged 3.8, 2.0, 0.42, and 0.04 ppt, respectively, and the 1995-1996 growth rates were 0.27, 0.06, 0.01, and 0.006 ppt yr<sup>-1</sup>, respectively. Total bromine in halons has increased by a factor of 10 since the late 1970s (Figure 1-4). While the growth rates of  $\text{CBrF}_3$  and  $\text{CBrF}_2\text{CBrF}_2$  are slowing,  $\text{CBrClF}_2$  continues to accumulate at a quasi-steady rate, and the  $\text{CBr}_2\text{F}_2$  growth rate is accelerating (SORG 1996; Fraser *et al.*, 1998). Based on a 2-D model calculation, global emissions of both  $\text{CBr}_2\text{F}_2$  and  $\text{CBrF}_2\text{CBrF}_2$  averaged about 0.7 to 0.8 Gg in 1997 (Fraser *et al.*, 1998). NOAA/CMDL and UEA halon data agree to within 10 to 15% for  $\text{CBrClF}_2$ ,  $\text{CBrF}_3$ , and  $\text{CBrF}_2\text{CBrF}_2$  (Table 1-2).

During the ASTEX/MAGE aircraft-based campaign over the NE Atlantic (30°N to 40°N, June 1992) region, average free tropospheric (2 to 3.5 km) values

for  $\text{CBrClF}_2$  and  $\text{CBrF}_3$  of 3.0 and 2.1 ppt, respectively, were found (Blake *et al.*, 1996b), in good agreement with the NH NOAA/CMDL data (Figure 1-4). Aircraft measurements at the tropical tropopause and in the NH troposphere during 1996 were also in good agreement with the NOAA/CMDL measurements and trends (Schauffler *et al.*, 1998a,b). NH (17.5°N, 44°N, and 69°N) upper tropospheric  $\text{CBrClF}_2$  and  $\text{CBrF}_3$  abundances (2 ppt and 1.7 ppt, respectively) and growth rates (3% yr<sup>-1</sup> and 8% yr<sup>-1</sup>, respectively) for 1990 have been derived from air samples collected by balloon between 1977 and 1993 (Fabian *et al.*, 1996). These data are consistent with the abundances and trends reported in Table 1-2.

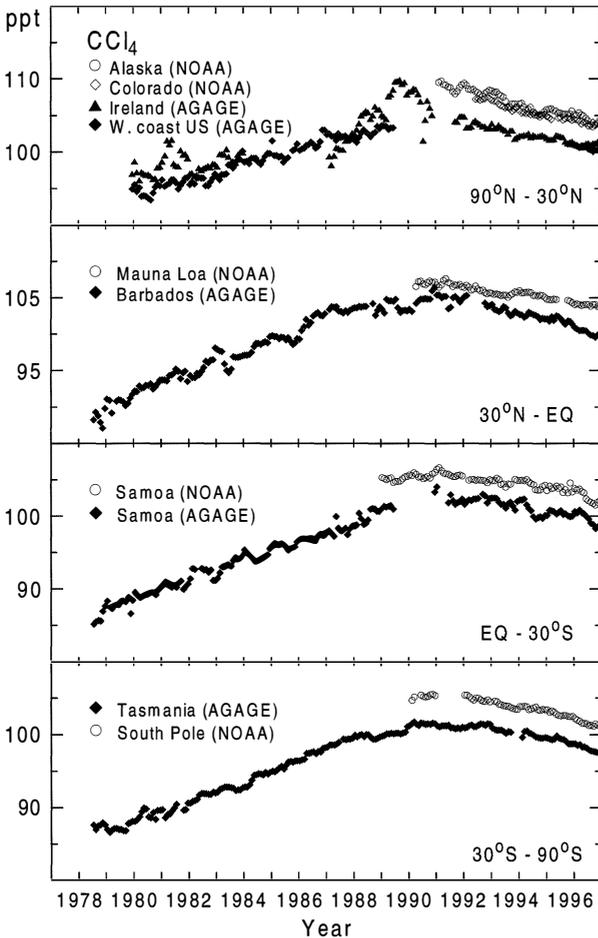
Measurements of halons have been performed in the upper troposphere and lower stratosphere both by in situ gas chromatograph (GC) ( $\text{CBrClF}_2$ ) and by whole air sampling techniques with subsequent GC analysis ( $\text{CBrF}_3$ ,  $\text{CBrF}_2\text{CBrF}_2$ ) (Wamsley *et al.*, 1998, and references therein). Significant correlations between the volume mixing ratios of each of these halon species and  $\text{CCl}_3\text{F}$  are observed. In stratospheric air masses approximately 6 years old, Wamsley *et al.* (1998) calculated that 98% of the organic bromine was converted into inorganic bromine ( $\text{Br}_y$ ), while Daniel *et al.* (1996) found somewhat less efficient conversion (90%) in air masses of average age between 5 and 6 years.

### 1.2.4 Carbon Tetrachloride ( $\text{CCl}_4$ )

In the 1994 Assessment, Sanhueza *et al.* (1995) reported  $\text{CCl}_4$  values in the GAGE (OGI) calibration scale (Simmonds *et al.*, 1988) that were about 20% higher than the new AGAGE (SIO) values reported here (Simmonds *et al.*, 1998). Data from a number of laboratories, from direct and indirect comparisons of standards, showed a wide range (25%) of  $\text{CCl}_4$  values (Fraser *et al.*, 1994), with the GAGE data being at the extreme high end of the range (the reasons for the high GAGE  $\text{CCl}_4$  calibration are unknown). With the introduction of the AGAGE calibration scale, there has been a significant improvement in the agreement between laboratories reporting  $\text{CCl}_4$  data, i.e., three laboratories making background  $\text{CCl}_4$  observations (SIO-AGAGE, NOAA/CMDL, UT) now agree to  $\pm 3\%$  (P. Fraser, CSIRO, Australia, personal communication of NOHALICE unpublished data, 1998).

NOAA/CMDL and ALE/GAGE/AGAGE  $\text{CCl}_4$  data are shown in Figure 1-5. In situ observations from the global ALE/GAGE/AGAGE network show that

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**Figure 1-5.** Monthly mean background data (in situ) for  $\text{CCl}_4$  mole fractions (ppt) from the NOAA/CMDL (Elkins *et al.*, 1996a; Montzka *et al.*, 1996; Elkins *et al.*, 1998) and ALE/GAGE/AGAGE (Simmonds *et al.*, 1998) global networks.

atmospheric concentrations of  $\text{CCl}_4$  reached a maximum in 1989-1990 (104 ppt) and have been decreasing by, on average,  $0.7 \text{ ppt yr}^{-1}$  throughout the 1990s, declining to 100 ppt in 1996 (Simmonds *et al.*, 1998). Data from the NOAA/CMDL in situ observational network show that atmospheric abundances of  $\text{CCl}_4$  declined steadily throughout the 1990s ( $-0.9 \text{ ppt yr}^{-1}$ ) and were 103 ppt in 1996 (Montzka *et al.*, 1996; Elkins *et al.*, 1996b; Elkins *et al.*, 1998).

During the ASTEX/MAGE aircraft-based campaign conducted over the NE Atlantic region ( $30^\circ\text{N}$  to  $40^\circ\text{N}$ , June 1992), an average lower tropospheric (2 to 3.5 km) volume mixing ratio of 110 ppt for  $\text{CCl}_4$  was measured by Blake *et al.* (1996b), which is similar (3 to

6% higher) to results from ground-based sampling at northern midlatitudes. Other measurements on air samples obtained via aircraft averaged 109 ppt in the northern midlatitudes during January to March 1992 (Daniel *et al.*, 1996).

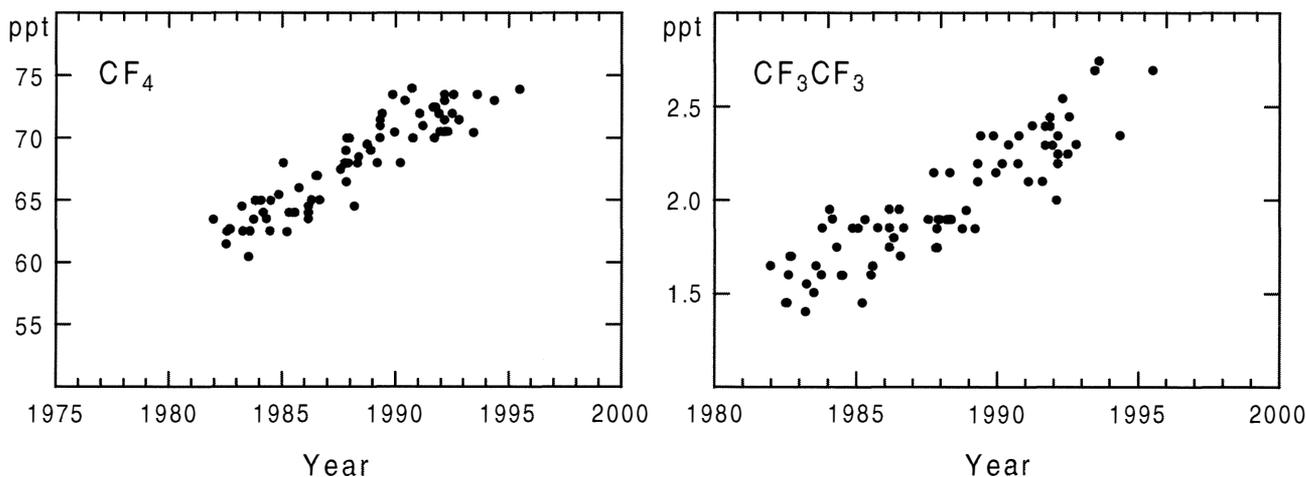
Lower stratospheric  $\text{CCl}_4$  mixing ratios derived from ATMOS/ATLAS-3 observations in November 1994 at northern latitudes are similar to the tropospheric  $\text{CCl}_4$  values reported above.  $\text{CCl}_4$  measurements obtained from an airborne GC during the ASHOE/MAESA campaign appear consistently lower than the ATMOS/ATLAS-3 measurements by some 15% (Chang *et al.*, 1996b; Elkins *et al.*, 1996b).

### 1.2.5 Perfluorocarbons (PFCs) and Sulfur Hexafluoride ( $\text{SF}_6$ )

PFCs and  $\text{SF}_6$  do not contribute to ozone depletion; however, they are very strong IR absorbers on a per-molecule basis and are very useful atmospheric tracers. Because of its long lifetime and monotonic growth in the atmosphere,  $\text{SF}_6$ , like carbon dioxide ( $\text{CO}_2$ ), has been used to estimate the mean age of a parcel of stratospheric air at the time of entry into the stratosphere (see Chapter 7). Harnisch *et al.* (1996a) have reconstructed tropospheric trends of the two very long-lived trace gases PFC-14 ( $\text{CF}_4$ ) and PFC-116 ( $\text{CF}_3\text{CF}_3$ ) from stratospheric vertical profiles by dating the air samples based on the measured  $\text{SF}_6$  mixing ratio (see Figure 1-6). NH tropospheric  $\text{CF}_4$  and  $\text{CF}_3\text{CF}_3$  abundances of 75 ppt and 2.6 ppt were obtained for the year 1995. From 1982 to 1995, the derived mean rates of increase for  $\text{CF}_4$  and  $\text{CF}_3\text{CF}_3$  were  $1.00 \pm 0.05 \text{ ppt yr}^{-1}$  and  $0.084 \pm 0.005 \text{ ppt yr}^{-1}$ , respectively, corresponding to accumulation rates of  $14.6 \pm 0.5 \text{ Gg yr}^{-1}$  and  $1.9 \pm 0.15 \text{ Gg yr}^{-1}$ , respectively.

From ATMOS solar occultation measurements at northern sub-tropical and midlatitudes during the ATLAS-3 shuttle mission of November 1994, Zander *et al.* (1996c) derived nearly constant volume mixing ratios of  $\text{CF}_4$  throughout the stratosphere ( $74 \pm 3 \text{ ppt}$ ). By comparing this value to the mean  $\text{CF}_4$  volume mixing ratio of  $63 \pm 4 \text{ ppt}$  measured during the ATMOS/Spacelab-3 mission (spring 1985), they derived an average annual increase for  $\text{CF}_4$  of  $1.6 \pm 0.6\% \text{ yr}^{-1}$  or  $1.1 \text{ ppt yr}^{-1}$  over the 9.5 years separating the two missions.

Atmospheric  $\text{SF}_6$  data in the 1990s have been inferred from NH and Southern Hemispheric (SH) oceanic surface water  $\text{SF}_6$  concentrations, assuming surface ocean-air equilibrium. When combined with other data from the 1970s and 1980s, it can be deduced



**Figure 1-6.** NH tropospheric  $\text{CF}_4$  and  $\text{CF}_3\text{CF}_3$  concentrations derived from  $\text{SF}_6$ -dated stratospheric air (Harnisch *et al.*, 1996a).

that atmospheric  $\text{SF}_6$  grew exponentially in the atmosphere through the 1970s (about  $30\% \text{ yr}^{-1}$ ) and linearly ( $0.16 \text{ ppt yr}^{-1}$ ) through the 1980s and 1990s, reaching 3 ppt in 1994 (Law *et al.*, 1994).

Direct measurements of  $\text{SF}_6$  in the global background atmosphere have been reported recently, including data obtained by analysis of the Cape Grim air archive (1978 to 1994). The global mean tropospheric abundance and growth rate in late 1994 were 3.3 ppt and  $0.23 \text{ ppt yr}^{-1}$  ( $6.9\% \text{ yr}^{-1}$ ) (Maiss *et al.*, 1996). Data from the NOAA/CMDL flask sampling network show that the global average abundance of  $\text{SF}_6$  in 1995 was 3.4 ppt, growing at  $0.23 \text{ ppt yr}^{-1}$  or  $6.8\% \text{ yr}^{-1}$  (Elkins *et al.*, 1996a). By mid-1996 the  $\text{SF}_6$  global background abundance reached 3.6 ppt and the global growth rate was  $0.24 \text{ ppt yr}^{-1}$  ( $6.7\% \text{ yr}^{-1}$ ) (Geller *et al.*, 1997). Laboratory inter-comparisons have shown that the NOAA/CMDL  $\text{SF}_6$  calibration scale is 1% lower than the University of Heidelberg scale (Maiss *et al.*, 1996; Geller *et al.*, 1997). The NOAA/CMDL and the University of Heidelberg  $\text{SF}_6$  data are shown in Figure 1-7.

By adopting an  $\text{SF}_6$  mixing ratio profile of the “no loss” type (Ko *et al.*, 1993),  $\text{SF}_6$  concentrations at the altitude of the ISSJ of 2.0, 3.1, and 4.4 ppt were found in 1988, 1992, and 1997, respectively, growing exponentially at  $8.3 \pm 0.5\% \text{ yr}^{-1}$  (Mahieu *et al.*, 1996). Compared with the surface mixing ratios measured at various NH sites (see Figure 1-7), the Jungfraujoch remote IR data are higher by 8 to 10%. A similar bias (5%) was reported by Chang *et al.* (1996b), when comparing measurements of  $\text{SF}_6$  (November 1994) from

the Space Shuttle-based ATMOS-FTIR and the ACATS-GC onboard the NASA ER-2 high-altitude aircraft. These differences are within the accuracy currently achievable for  $\text{SF}_6$  analysis by remote sensing in the IR (Abrams *et al.*, 1996a).

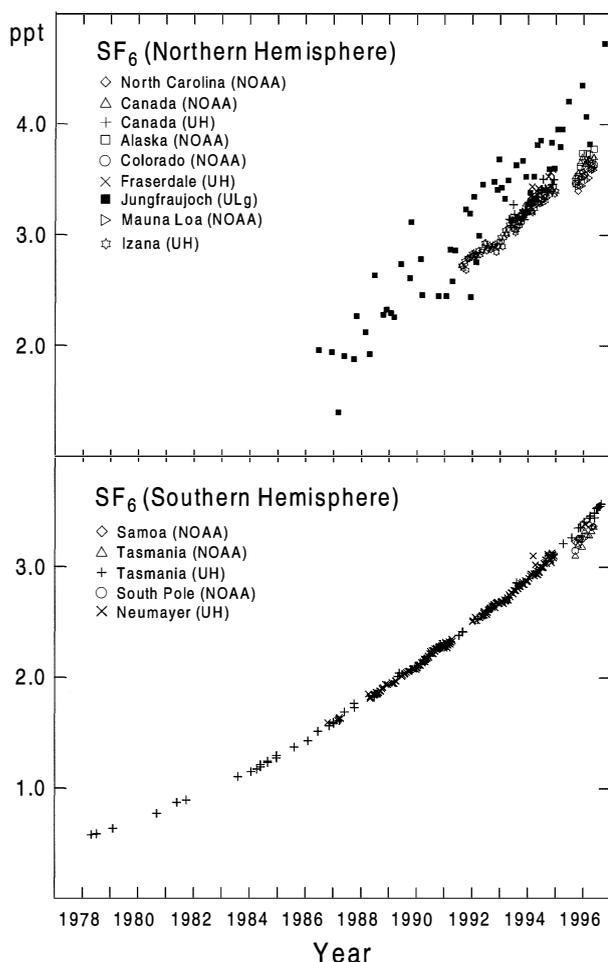
Based on the comparison of  $\text{SF}_6$  mixing ratio profiles measured in the lower stratosphere by ATMOS during spring 1985 and fall 1994, Rinsland *et al.* (1996a) derived an increase of  $8.0 \pm 0.7\% \text{ yr}^{-1}$ , in good agreement with the increases cited above. Furthermore, a comparison of the 1985 ATMOS measurements of  $\text{SF}_6$  with those made during a balloon flight in September 1993 (Sen *et al.*, 1996) indicates an  $\text{SF}_6$  growth rate of  $8.1 \pm 0.7\% \text{ yr}^{-1}$  in the 18- to 24-km region. These are in very good agreement with the early 1990  $\text{SF}_6$  rate of increase of  $8.3\% \text{ yr}^{-1}$  reported by Maiss and Levin (1994).

### 1.2.6 Nitrous Oxide ( $\text{N}_2\text{O}$ )

$\text{N}_2\text{O}$  is the major source of stratospheric  $\text{NO}_x$ , which is involved in catalytic ozone destruction (see Chapters 6 and 7). Long-term changes in  $\text{N}_2\text{O}$  sources, primarily anaerobic processes in the soils and oceans, and secondarily industrial activity, will therefore impact the ozone layer.

Global average  $\text{N}_2\text{O}$  concentrations have increased steadily in the troposphere from an estimated 275 ppb in preindustrial times (Machida *et al.*, 1995; Battle *et al.*, 1996) to 299 ppb by 1976 and 311 to 312 ppb by 1996 (Elkins *et al.*, 1998; Prinn *et al.*, 1990, 1998). The mean trend was  $+0.25\% \text{ yr}^{-1}$  during the 1980s, with substantial

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**Figure 1-7.** Global SF<sub>6</sub> data measured in the Cape Grim air archive (UH) (Maiss *et al.*, 1996) and in the global flask network of NOAA/CMDL (Geller *et al.*, 1997). Spectroscopic data from ISSJ (Jungfraujoch, ULg) are shown by filled squares in the upper frame (Mahieu *et al.*, 1996).

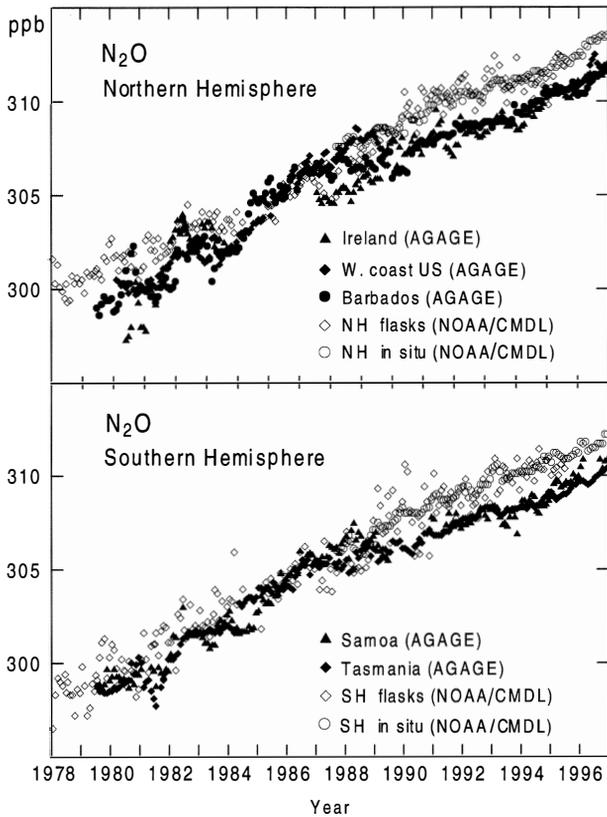
year-to-year variations. More recently, the growth rate of N<sub>2</sub>O decreased from about 1 ppb yr<sup>-1</sup> in 1991 to 0.5 ppb yr<sup>-1</sup> in 1993. The cause of this decrease is unknown, but global reductions in the use of nitrogenous fertilizer, post-Pinatubo temperature reductions and their effect on soil N<sub>2</sub>O production and reduced tropical oceanic upwelling of N<sub>2</sub>O-rich waters have been suggested (Thompson *et al.*, 1994). Another possibility is that the trend was influenced by stratospheric circulation changes induced by volcanic aerosols from Mt. Pinatubo (Schauffler and Daniel, 1994). By 1995, the growth rate

had increased again to 0.6 ppb yr<sup>-1</sup> (Elkins *et al.*, 1996a).

In situ N<sub>2</sub>O data from the ALE/GAGE/AGAGE network (1979-1996) and NOAA/CMDL flask and in situ N<sub>2</sub>O data (1978-1996) are shown in Figure 1-8 (Prinn *et al.*, 1990, 1998; Elkins *et al.*, 1996a, 1998). In general the NOAA/CMDL data are higher than the ALE/GAGE/AGAGE data by 1 to 2 ppb, except in the mid- to late-1980s, when N<sub>2</sub>O observations from both networks were similar for similar latitudes. The GAGE N<sub>2</sub>O data at Cape Grim, Tasmania, appear to have unresolved calibration problems during the 1980s (P. Fraser, CSIRO, Australia, personal communication of unpublished data, 1998), which may apply to the entire GAGE network during this period.

Vertical column abundances of N<sub>2</sub>O, monitored remotely above the ISSJ by IR solar observations, show a long-term trend of  $0.36 \pm 0.06\% \text{ yr}^{-1}$  for the period 1984 to 1992 (Zander *et al.*, 1994b). This trend reduced slightly, when evaluated over the 1984 to 1996 period, to  $0.33 \pm 0.04\% \text{ yr}^{-1}$ . This latter value is higher than the mean increase ( $0.25\% \text{ yr}^{-1}$ ) derived from ground-based in situ measurements. This may be due to a rise of the tropopause by about 150 m during the 12-year period of ISSJ measurements. Such a rise can result from either warming of the troposphere and/or cooling of the lower stratosphere. The magnitude of the rise required to reconcile the column and ground-based increases of N<sub>2</sub>O is similar to the rise that is deduced from long-term series of ozone and temperature measurements at Hohenpeissenberg, Germany (Claude and Steinbrecht, 1996; Steinbrecht *et al.*, 1998).

In the 1994 Assessment, Sanhueza *et al.* (1995) estimated the annual global N<sub>2</sub>O source to be 6 to 19 Tg (N) yr<sup>-1</sup> and the sinks plus atmospheric accumulation to be 12 to 22 Tg (N) yr<sup>-1</sup>. A more recent international assessment of N<sub>2</sub>O sources and sinks was carried out for the Intergovernmental Panel on Climate Change (IPCC) (Prather *et al.*, 1995). The global N<sub>2</sub>O source was estimated to be 10 to 17 Tg (N) yr<sup>-1</sup>, of which 4 to 8 Tg (N) yr<sup>-1</sup> was of anthropogenic origin, and total sinks plus atmospheric accumulation were 13 to 20 Tg (N) yr<sup>-1</sup>. Bouwman *et al.* (1995) estimated a similar global N<sub>2</sub>O source of 11 to 17 Tg (N) yr<sup>-1</sup>. They identified several sources not considered in the IPCC budget, including N<sub>2</sub>O formation from atmospheric ammonia (NH<sub>3</sub>) oxidation, and N<sub>2</sub>O emissions from soil waters and from soil N deposited from the atmosphere. At least 40% of sources evaluated by Bouwman *et al.* (1995) were subject to anthropogenic influence. Recently there have been



**Figure 1-8.** Monthly mean  $N_2O$  data from the ALE/GAGE/AGAGE (in situ) and NOAA/CMDL (flask and in situ) global networks (Prinn *et al.*, 1990, 1998; Elkins *et al.*, 1996a, 1998).

upward revisions in the strength of various agricultural sources (Berges and Crutzen, 1996; Nevison and Holland, 1997; Mosier and Kroeze, 1998). With these revisions, the central value of the total sources ( $16 \text{ Tg (N) yr}^{-1}$ ) (Mosier and Kroeze, 1998) now matches the estimates of the total of atmospheric removal ( $12 \text{ Tg (N) yr}^{-1}$ ) and atmospheric increase ( $4 \text{ Tg (N) yr}^{-1}$ ).  $N_2O$  emissions from agricultural systems worldwide have increased from  $3.4 \text{ Tg (N) yr}^{-1}$  in 1960 to  $6.2 \text{ Tg (N) yr}^{-1}$  in 1994, a growth rate of  $1$  to  $2\% \text{ yr}^{-1}$  (Mosier and Kroeze, 1998).

Isotopic studies (Kim and Craig, 1993; Johnston *et al.*, 1995; Rahn and Whalen, 1997), and a previously (perhaps wrongly) implied imbalance between  $N_2O$  sources and sinks, have led to suggestions of a significant stratospheric source of  $N_2O$  (Prasad, 1994; McElroy and Jones, 1996; Prasad *et al.*, 1997), possibly as large as 25% of the biological  $N_2O$  source (Prasad, 1997).

However, recently, Yung and Miller (1997) have been able to explain the stratospheric isotopic behavior of  $N_2O$  without invoking stratospheric  $N_2O$  sources. The ocean could also be a source of isotopically enriched  $N_2O$  (Yoshinari *et al.*, 1997).

### 1.2.7 Regional Studies

The abundance and trend data on long-lived trace gases discussed above have been selected to be representative of large (hemispheric to global) space scales. However long-term or large-scale regional studies of trace gases can also provide useful information on regional trends and on regional emissions.

Estimates of the recently declining emissions of  $CCl_3F$ ,  $CCl_2F_2$ ,  $CCl_2FCClF_2$ ,  $CH_3CCl_3$ , and  $CCl_4$  from Europe have been made using selected in situ AGAGE data from Ireland (Simmonds *et al.*, 1993, 1996). From 1987 to 1994, emissions of the CFCs from Europe fell by a factor of 5,  $CH_3CCl_3$  by a factor of 2, and  $CCl_4$  by a factor of 4. The European source of  $N_2O$  ( $1$  to  $2 \text{ Tg (N) yr}^{-1}$ ) does not appear to exhibit a trend.

In situ AGAGE  $N_2O$  observations from Cape Grim, Tasmania, have been used to estimate SE Australian fluxes of  $N_2O$  from 1985 to 1993, which exhibit a significant dependence on rainfall (Wilson *et al.*, 1997).

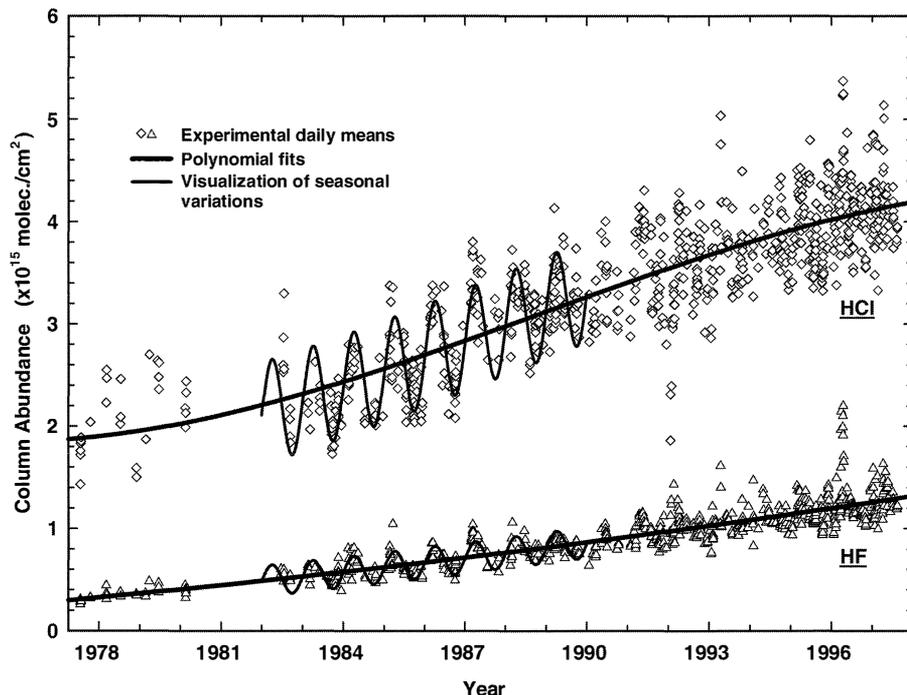
Trends of  $CCl_3F$ ,  $CCl_2F_2$ ,  $CCl_2FCClF_2$ ,  $CCl_4$ , and  $SF_6$  ( $-0.8$ ,  $5.4$ ,  $1.8$ ,  $-1.4$ , and  $0.25 \text{ ppt yr}^{-1}$  respectively), which are in good agreement with recent trends of remote background mixing ratios in the NH, have been deduced from in situ NOAA/CMDL data collected on a tall tower (610 m) in North Carolina, U.S., (Hurst *et al.*, 1997).

An  $SF_6$  longitudinal transect has been obtained along the 9000-km Trans-Siberian railway. The data show the eastward dilution of the European-sourced  $SF_6$  emission plume and local Russian  $SF_6$  sources (Crutzen *et al.*, 1998).

### 1.2.8 Hydrogen Fluoride (HF) and Hydrogen Chloride (HCl)

HF is the ultimate inorganic sink for stratospheric fluorine atoms resulting from the photodissociation of fluorinated organic source gases transported into the stratosphere. The detection of atmospheric HF in the mid-1970s and subsequent rapid growth of HF over the last two decades are consistent with its production resulting from the decomposition of anthropogenic CFCs. As no significant natural sources of HF in or to the

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**Figure 1-9.** Evolution of the daily mean column abundances of HF and HCl above the Jungfraujoch during the last two decades (Zander *et al.*, 1998). Overall fits to the data are shown by solid lines. The sinusoids (drawn only over a limited period for clarity) reflect observed seasonal variations in both columns. Significant short-term variability is observed during the winter-spring period, primarily associated with intrusions of high-latitude air masses.

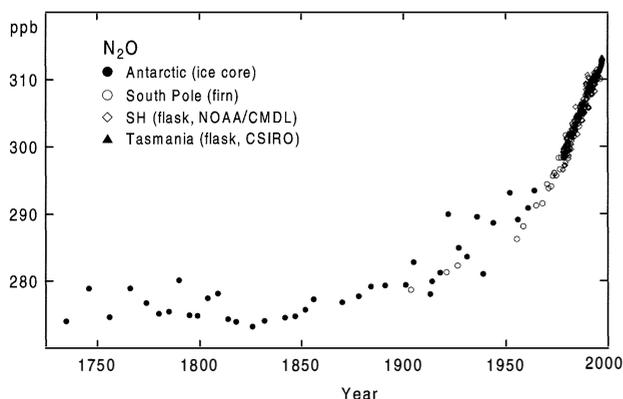
atmosphere have been identified, the HF loading is an indicator of the total abundance and mix of CFCs, HCFCs, and HFCs in the atmosphere and its exceptional stability in the stratosphere makes it an excellent tracer of latitudinal and vertical transport and dynamics (Chipperfield *et al.*, 1997). In addition to HF, carbonyl fluoride ( $\text{COF}_2$ ) and chlorofluorocarbonyl (COCIF) are important for inorganic fluorine budget evaluations.

On a global basis, HCl is the major reservoir for inorganic stratospheric chlorine resulting from the breakdown of chlorinated organics.

Analyses of IR solar observations at the ISSJ since 1977 indicate a steady increase in the HF vertical column abundance above this northern midlatitude NDSC site (see Figure 1-9) from  $0.29 \times 10^{15}$  molecules  $\text{cm}^{-2}$  in 1977 to  $1.22 \times 10^{15}$  molecules  $\text{cm}^{-2}$  in 1997; this amounts to an exponential increase of  $7.2\% \text{ yr}^{-1}$ , or a mean HF burden increase of  $0.47 \times 10^{14}$  molecules  $\text{cm}^{-2} \text{ yr}^{-1}$ . The steady HF column increase above ISSJ contrasts with the slowing down of the HCl column growth rate from  $(1.9 \pm 0.2) \times 10^{14}$  molecules  $\text{cm}^{-2} \text{ yr}^{-1}$  between 1984 and

1989 to  $(1.0 \pm 0.2) \times 10^{14}$  molecules  $\text{cm}^{-2} \text{ yr}^{-1}$  from mid-1991 to mid-1996 (Zander *et al.*, 1998). These changes result from the recent reduction of CFC releases as set out in the Montreal Protocol and related Amendments, and subsequent CFC replacements by HCFCs and HFCs. A recently published record of stratospheric column measurements of HCl above Kitt Peak National Solar Observatory (KPNSO) (Wallace and Livingstone, 1997) is consistent with an increase of  $0.74 \times 10^{14}$  molec  $\text{cm}^{-2} \text{ yr}^{-1}$  over the 1971 to 1997 period, with some indication of a slowing down during the latter years.

Since the previous Assessment (WMO, 1995), some space-based experiments have added significantly to the quantification and understanding of the chlorine and fluorine loading in the stratosphere. Among these is the ATMOS FTIR experiment flown aboard the Space Shuttle in 1985, 1992, 1993, and 1994 (Gunson *et al.*, 1996) as part of the ATLAS program (Kaye and Miller, 1996). From the first and last ATMOS deployments, it was found that the concentration of HCl in the upper stratosphere (above 1 mbar) increased from a mean 2.5



**Figure 1-10.** Mole fractions of  $\text{N}_2\text{O}$  (ppb) for the past 250 years inferred from firn air (blue) (Battle *et al.*, 1996), air in Antarctic ice (red) (Machida *et al.*, 1995), in flask samples collected at SH sites and measured by NOAA/CMDL (purple) (Elkins *et al.*, 1996a) and in flasks collected at Cape Grim, Tasmania and measured by CSIRO (green) (Langenfelds *et al.*, 1996; Steele *et al.*, 1996).

$\pm 0.1$  ppb in April to May 1985, to a mean  $3.5 \pm 0.2$  ppb in November 1994; this 9.5-year change corresponds to an annual growth rate of HCl equal to  $3.5\% \text{ yr}^{-1}$ , or a mole fraction increase of  $105 \text{ ppt yr}^{-1}$  (Zander *et al.*, 1992; 1996b).

Over that same 9.5-year period, the ATMOS measurements indicate that the upper stratospheric HF concentration increased by almost a factor of 2, from a mean  $0.76 \pm 0.08$  ppb to  $1.50 \pm 0.15$  ppb, corresponding to a growth rate of  $7.2\% \text{ yr}^{-1}$  or  $78 \text{ ppt yr}^{-1}$  (Zander *et al.*, 1992; Abrams *et al.*, 1996b). From a global time series of satellite (UARS/HALOE) observations of HCl and HF in the stratosphere between October 1991 and April 1995, Russell *et al.* (1996c) found increases near 55 km of  $102 \pm 6$  and  $72 \pm 2 \text{ ppt yr}^{-1}$ , respectively. While the ATMOS and HALOE trends are in good agreement, the HALOE HCl and HF concentrations tend to be lower throughout the stratosphere than those obtained by ATMOS (Russell *et al.*, 1996a,b; Liu *et al.*, 1996; Achard *et al.*, 1997). However, a revision of the HALOE databases for HCl and HF has significantly improved this situation (J.M. Russell III, Hampton University, U.S., personal communication, 1998; also, <http://haloedata.larc.nasa.gov/HALOE/home.html>). Based on these revised data, Considine *et al.* (1997) analyzed monthly average concentrations of HF above 55 km altitude over the  $50^\circ\text{N}$  to  $50^\circ\text{S}$  latitude band and found that the rate of increase

of HF in the lower mesosphere has definitely slowed down, in a manner consistent with the tropospheric loadings and trends of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  in the early 1990s (Montzka *et al.*, 1996; Cunnold *et al.*, 1997). A similar analysis scheme has been applied to the revised HALOE HCl time series of the past years (Considine *et al.*, 1998); it also indicates a definite slowdown of the HCl concentration above 55 km altitude, in a manner consistent with the decreasing rate of tropospheric chlorine (Cl) loading reported by Montzka *et al.* (1996).

### 1.2.9 Preindustrial Atmospheric Abundances

While increases of the atmospheric abundance of  $\text{CF}_4$  and  $\text{CF}_3\text{CF}_3$  in recent decades can be attributed to the electrolytic production of aluminum, ice core studies indicate that there is an additional source of  $\text{CF}_4$  predating aluminum production (Harnisch *et al.*, 1996a,b). Both ice core and air archive studies indicate that the pre-industrial atmospheric background level was about 40 ppt (Harnisch *et al.*, 1996b). Natural fluorites and granites are found to exhibit mass contents of up to  $10^{-9}$  of  $\text{CF}_4$ ,  $\text{SF}_6$ , and  $\text{CClF}_3$  and, due to weathering and crustal metamorphism, 100 to 5000 kg of these substances are naturally released annually from the Earth's crust into the atmosphere (Harnisch and Eisenhauer, 1998). From extrapolated crustal abundances of these gases and their atmospheric lifetimes, Harnisch and Eisenhauer (1998) concluded that natural atmospheric background levels of about 40 ppt  $\text{CF}_4$ , less than 0.05 ppt of  $\text{SF}_6$ , and less than 0.005 ppt of  $\text{CClF}_3$  can be expected from this source.

A precise record of atmospheric  $\text{N}_2\text{O}$  levels throughout this century has been obtained from air trapped in Antarctic glacial firn. Firn air ages are determined from correlation of the  $\text{CO}_2$  mole fractions in the firn samples with the atmospheric  $\text{CO}_2$  history as determined by Etheridge *et al.* (1996). Because  $\text{CO}_2$  and  $\text{N}_2\text{O}$  are assumed to have the same diffusivities in firn,  $\text{CO}_2$  ages also apply to  $\text{N}_2\text{O}$ . In the early 1900s,  $\text{N}_2\text{O}$  levels were about 280 ppb (see Figure 1-10). During the first half of this century the atmospheric mole fraction grew at  $(0.06 \pm 0.01)\% \text{ yr}^{-1}$ , reaching about 290 ppb by the early 1960s. Thereafter  $\text{N}_2\text{O}$  increased more rapidly at  $(0.22 \pm 0.02)\% \text{ yr}^{-1}$  to contemporary SH values of around 310 ppb (Machida *et al.*, 1995; Elkins *et al.*, 1996a; Battle *et al.*, 1996).

In the preindustrial period (i.e., before significant release of industrial halocarbons, including CFCs, occurred), chlorine-containing gases (such as methyl

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chloride) were emitted to the atmosphere from natural processes. Assuming that the preindustrial HCl levels can be related to non-CFC organochlorine releases and that all HF originates from CFCs, correlation plots of simultaneously measured HCl and HF column abundances during the 1970s and 1980s indicate that the preindustrial HCl column abundances, corresponding to zero HF abundances, were  $(0.90 \pm 0.15) \times 10^{15}$  molecules  $\text{cm}^{-2}$  above the KPNSO (Rinsland *et al.*, 1991; Wallace and Livingstone, 1991, 1997) and  $(0.70 \pm 0.10) \times 10^{15}$  molecules  $\text{cm}^{-2}$  above ISSJ (Zander *et al.*, 1996d). The relative difference results from KPNSO being located at 2.06 km and ISSJ at 3.58 km, indicating that most of that HCl resided in the troposphere.

### 1.3 THE BUDGETS OF CHLORINE, BROMINE, AND FLUORINE

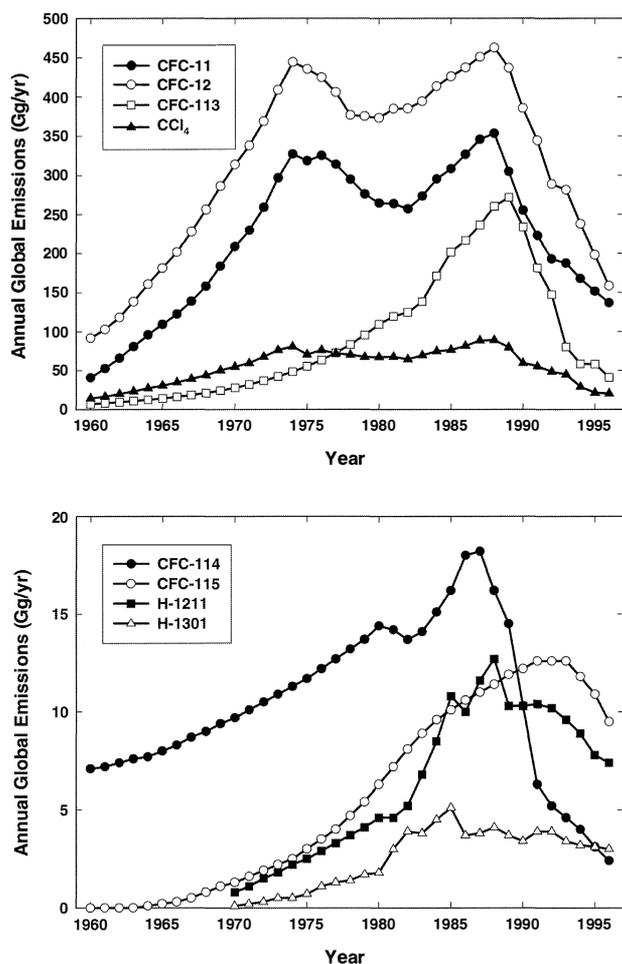
#### 1.3.1 Background

Organic compounds containing bromine, chlorine, fluorine, and iodine are released at the Earth's surface, mix rapidly, and are exchanged between hemispheres in the troposphere. Whereas most of these compounds originate predominantly from human activities, natural biological and chemical processes can also contribute to the total organic budget (WMO, 1995). Some of these organics (e.g.,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{Cl}$ , HFCs, HCFCs) that contain hydrogen are destroyed by reaction with the hydroxyl radical (OH) in the troposphere. For these compounds (see Chapter 2), their atmospheric lifetimes and their effect on stratospheric ozone depletion are reduced compared to similar compounds (i.e., CFCs and halons) that are fully halogenated. Transport time scales are important in describing when stratospheric ozone losses can be expected to occur and can be estimated from observations of long-lived trace gases (like  $\text{CO}_2$  (Boering *et al.*, 1996),  $\text{SF}_6$  (Elkins *et al.*, 1996b), and CFC-115 (Daniel *et al.*, 1996)) and from atmospheric models (Mahowald *et al.*, 1997; Hartley *et al.*, 1994). Mixing within a hemisphere occurs in the troposphere on time scales of a few weeks to three months, whereas exchange between hemispheres occurs between 1.1 and 1.7 years (Levin and Hesshaimer, 1996; Geller *et al.*, 1997). The halocarbons also are transported into the stratosphere, where photolysis and reaction with OH lead to the formation of inorganic species of bromine, chlorine, and fluorine. Mixing between the troposphere

and the lower and middle stratosphere, where most of the ozone depletion occurs, takes place within 1 to 3 years in the tropics and between 3 to 6.5 years at midlatitudes and in the polar regions at altitudes of 21 km and below (Elkins *et al.*, 1996b; Harnisch *et al.*, 1996a; Waugh *et al.*, 1997; Volk *et al.*, 1997; Wamsley *et al.*, 1998). Mean ages of an air parcel deduced from observations of  $\text{SF}_6$  over different latitudes and altitudes from October through November 1994 demonstrate these mixing times (Volk *et al.*, 1997; Wamsley *et al.*, 1998). The inorganic species can form compounds that either react with stratospheric ozone (reactive species) or do not react (nonreactive species, also called reservoirs). Volcanic eruptions inject inorganic chlorine ( $\text{Cl}_y$ ) into the atmosphere, primarily in the form of HCl; however, most of it is rained out in the troposphere and very little reaches the stratosphere (Tabazadeh and Turco, 1993; Russell *et al.*, 1996c; Zander *et al.*, 1996a; Coffey 1996). Under normal stratospheric conditions, oxides of nitrogen, primarily NO and  $\text{NO}_2$ , can temporarily tie up both bromine and chlorine atoms in nonreactive reservoirs such as bromine nitrate ( $\text{BrONO}_2$ ) and chlorine nitrate ( $\text{ClONO}_2$ ), but these atoms can be freed efficiently in the presence of sulfate aerosols and polar stratospheric clouds, leading to enhanced local ozone depletion. So far, inorganic fluorine and iodine have not contributed to any appreciable ozone depletion, the former because of the stability of its ultimate sink, HF (Stolarski and Rundel, 1975), and the latter because of its low concentration in the atmosphere (Wennberg *et al.*, 1997).

#### 1.3.2 Anthropogenic Sources of Atmospheric Chlorine, Bromine, and Fluorine

Worldwide emissions of halocarbons have changed dramatically in recent years. With the implementation of the Montreal Protocol on Substances that Deplete the Ozone Layer and its Amendments, production in developed countries ceased by the end of 1993 for halons and by the end of 1995 for CFCs,  $\text{CCl}_4$ , and  $\text{CH}_3\text{CCl}_3$  (see Chapter 2), apart from a comparatively small amount for essential uses and an allowance to supply the needs of developing countries, which have a ten-year grace period. The evidence from production statistics is that compliance with the Montreal Protocol is proceeding either on or ahead of schedule and CFC production in the major industrialized nations is now below the level of the early 1960s (AFEAS, 1998; UNEP, 1997).



**Figure 1-11.** Annual global emissions (in  $\text{Gg yr}^{-1}$ ) of long-lived halocarbons estimated by industry from audited production, sales, and other data (AFEAS, 1998; Fisher *et al.*, 1994; McCulloch, 1992; Fraser *et al.*, 1998; updated by P. Midgley, personal communication).

Emissions of the controlled substances continue from the permitted, comparatively small use in developing countries and also, more significantly, from the slow release of halocarbons held in existing equipment and plastic foams. Nevertheless, worldwide emissions of halocarbons have declined dramatically in recent years (see Figure 1-11). Although illegal imports of CFCs, estimated to be some 10 Gg, may be affecting the market for CFC alternatives in developed countries, their effect on CFC emissions and chlorine loading is estimated to be significantly less, by about a factor of 10, than that from legal use (SORG, 1996).

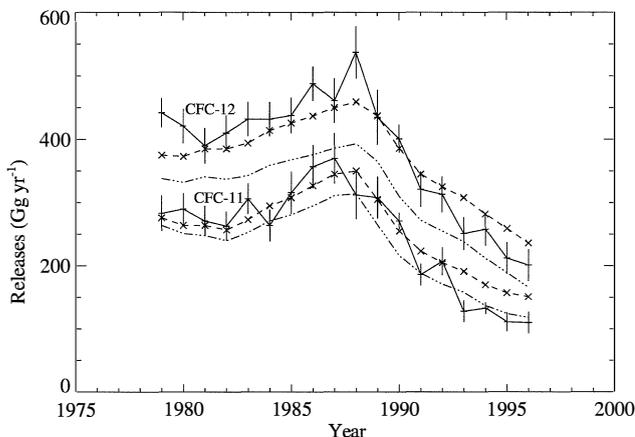
### 1.3.2.1 CFCs

The most detailed compilation of the annual production and sales of individual CFCs in recent years is the industrial survey issued by the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS). The survey participants, located in Europe, North America, and Japan, together with their subsidiaries elsewhere in the world, provide essentially complete global coverage for the early years of production. Subsequently, production not reported by AFEAS began elsewhere, primarily in India, China, and Russia. It has been estimated, however, that AFEAS inventories cover over 90% of the global production until the mid-1980s, and still about 80% of the much-diminished global total for the major products (CFC-11 and -12) as late as 1993 (Fisher *et al.*, 1994; UNEP, 1997). Currently, production in the industrialized nations has been phased out except for the minor amount permitted for essential internal uses and CFCs exported to supply the needs of developing countries. The Montreal Protocol permits up to 15% of base year 1986 production, amounting to some 160 Gg of combined CFCs, for this export market. Consequently, production reported to AFEAS now represents a much smaller fraction of the global total, around 60% from 1994 to 1995.

The databases compiled by UNEP provide a detailed geographical breakdown with potentially complete global coverage, but it takes a long time for all national returns to come in. UNEP publishes totals of aggregated CFC production on an Ozone Depletion Potential-weighted basis with no sales breakdown. In order to get global emission numbers for individual compounds, it is necessary to combine these two UNEP datasets and this has been done to calculate the global emissions shown in Figure 1-11 (Fisher *et al.*, 1994; McCulloch *et al.*, 1994; Fraser *et al.*, 1998; P.M. Midgley, M & D Consulting, Germany, personal communication, 1998).

Industrial sales of CFCs have declined rapidly in recent years; surveys of the world's major producers show that sales in 1995 were 32 Gg, 83 Gg, and 23 Gg, respectively, for the major products CFC-11, -12, and -113. These were less than 10% of the amounts reported in the years of peak production for CFC-11 and -113, and less than 20% for CFC-12 (AFEAS, 1998). Calculated emissions of CFC-113 are also less than 10% of the peak year (1989) for this compound; its main application as a solvent results in its rapid emission

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**Figure 1-12.** Global yearly releases of CFC-11 and CFC-12 ( $\text{Gg yr}^{-1}$ ) estimated from the ALE/GAGE/AGAGE measurements assuming lifetimes of 50 and 110 years, respectively (solid lines and plus symbols; Cunnold *et al.*, 1997). Also shown are industry estimated emissions from reporting companies only (3 dots and dash line) and world releases including reporting and nonreporting companies (dashed lines joining crosses) estimated by Cunnold *et al.* (1997).

(Fisher and Midgley, 1993). The principal uses of CFC-11 and -12, namely, foam blowing, refrigeration, and air conditioning, all involve delays between CFC use and its release to the atmosphere (Fisher and Midgley, 1994). A large fraction of emissions comes from the bank of previously used CFCs held in equipment and foams. Therefore, the reductions in calculated emissions lag behind those in reported sales, being less in 1995 than 40% of the peak year (1974) for CFC-11 and 45% for CFC-12. Total consumption of CFCs in developing countries operating under Article 5 of the Montreal Protocol was about 170 Gg in 1994 (UNEP, 1997). It has been estimated that about half of these requirements were met by production in the developing countries themselves and the rest by material exported from developed countries (UNEP, 1994). Consumption in developing countries will be phased out by 2010.

Modeled atmospheric mixing ratios for CFC-11 and CFC-12 from emission estimates by industry tend to overestimate the recent mixing ratios and trends from both the NOAA/CMDL and AGAGE global networks (Elkins *et al.*, 1993; Cunnold *et al.*, 1994, 1997; Montzka *et al.*, 1996). As an example, Figure 1-12 reproduces

the comparison between the global yearly releases estimated from the ALE/GAGE/AGAGE measurements and estimates from industry using reporting companies and world releases versus time. The inconsistency during the last years (Cunnold *et al.*, 1997) cannot be explained by errors in lifetimes (e.g., by using the WMO (1998) values recommended in Table 1-1) because atmospheric data show the growth rate declining more rapidly in recent times. Possible reasons may be changing emission factors for various uses, overestimates of the banked reservoir, or inaccurate estimates of emissions for nonreporting companies. In Figure 1-12, the non-reporting company emissions have been held constant in recent years, primarily because of lack of other information. One interpretation of the results is that nonreporting company emissions have dropped in recent years.

### 1.3.2.2 HALONS

The production of Halon-1211 and -1301 peaked in 1988 and ceased in the developed world at the end of 1993 under the provisions of the Montreal Protocol. Production is known to occur in developing countries (e.g., China, India, Korea) and is permitted until 2002. However, large quantities of these gases, which are used as specialized fire extinguishing agents, are stored (banked) in equipment and emissions come predominantly from this bank. Using a combination of audited industry data and national data reported to the UNEP, estimates have been made of the annual emissions of Halon-1211 and -1301 (McCulloch, 1992; UNEP, 1997). To illustrate the size and growth of the bank, production of Halon-1211 in 1988 was 20 Gg, emissions were about 13 Gg, but the bank was 49 Gg and grew by 1994-1996 to an estimated 60 Gg. The equivalent figures for Halon-1301 were 8 Gg for 1988 production, 4 Gg for 1988 emissions, 60 Gg for the 1988 bank, and 70 Gg for the 1994-1996 bank (A. McCulloch, ICI Chemicals and Polymers Limited, U.K., personal communication, 1998; SORG, 1996).

Measured abundances of Halon-1211 and -1301 (Butler *et al.*, 1998) are lower than those derived from estimates of emissions by factors of about 0.75 and 0.97, respectively (see Figure 1-13). A simulation adjusting the atmospheric lifetime of Halon-1211 from 20 to 10 years produces a good fit between emission estimates (see Figure 1-11; also Fraser *et al.*, 1998) and measurements prior to 1993. This lower lifetime estimate

is consistent with photolysis results calculated in the troposphere and stratosphere (see Section 1.4.4), but inconsistent with the observed interhemispheric ratio of Halon-1211 (Butler *et al.*, 1998). The cause of the discrepancy between emissions and measurements of Halon-1211 is not fully understood at this time.

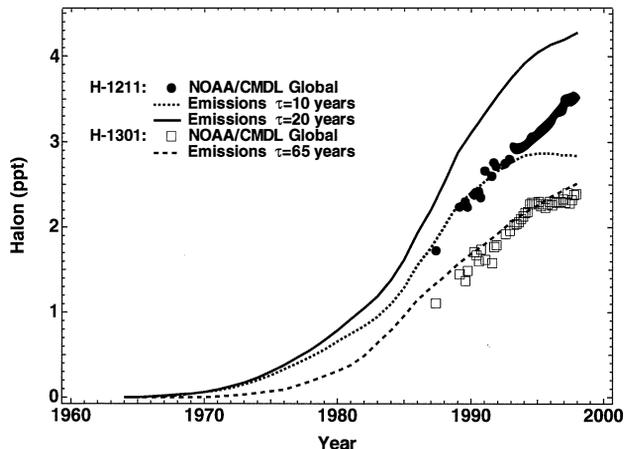
For Halon-2402, which was manufactured almost exclusively in eastern Europe, reports to UNEP show production of about 4 Gg in 1986, falling to less than 10% of this total in 1994 to 1995 (UNEP, 1997). On the other hand, not much is known about the production of Halon-1202, which is used as a fire extinguishing agent only in military transport aircraft and is not covered by UNEP reports (SORG, 1996).

### 1.3.2.3 CARBON TETRACHLORIDE (CCl<sub>4</sub>)

Emissions of CCl<sub>4</sub> into the atmosphere, which arise during its use as a chemical feedstock for CFC-11 and -12, and during the manufacture of CCl<sub>4</sub> itself, have decreased roughly in proportion to the decline in CFC production. Neither the quantities of CCl<sub>4</sub> produced nor the losses are recorded specifically but analysis of the UNEP data in combination with the AFEAS reports on CFC production can be used to derive CCl<sub>4</sub> emissions. These had declined to about 20 Gg yr<sup>-1</sup> by 1995 (A. McCulloch, ICI Chemicals and Polymers Limited, U.K., personal communication, 1998). The minor uses of CCl<sub>4</sub> as a process agent are also controlled under the Montreal Protocol and give rise to much lower emission totals (UNEP, 1995). Using an atmospheric lifetime for CCl<sub>4</sub> of 42 ± 12 years, Simmonds *et al.* (1998) found that ALE/GAGE/AGAGE atmospheric measurements and industry estimates were consistent if nonreporting countries are dominating world releases after a sharp drop in production in 1991 by reporting countries. However if the lifetime of CCl<sub>4</sub> is 35 years as recommended in Table 1-1, then the industrial emission scenario provided in Simmonds *et al.* (1998) underestimates emissions by about 17%.

### 1.3.2.4 OTHER COMPOUNDS

Estimated industrial emissions of the shorter lived organic compounds like CH<sub>3</sub>CCl<sub>3</sub>, selected HCFCs, and HFCs are presented in Chapter 2. While there are currently no available yearly emissions from industry for compounds composed mainly of fluorine (i.e., CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, ...), atmospheric measurements and simple atmospheric models can provide important confirmation



**Figure 1-13.** Atmospheric history of Halon-1211 and -1301 from NOAA/CMDL measurements and modeled emissions. Global average concentrations for Halon-1211 and -1301 are shown as filled circles and gray open squares, respectively. Lines are emission-based predictions (Figure 1-11; Fraser *et al.*, 1998), using atmospheric lifetimes given in the previous WMO Assessment (Solomon *et al.* in WMO, 1995), i.e., 20 years for Halon-1211 (solid black line) and 65 years for Halon-1301 (dashed gray line). The black dotted line represents concentration predictions for Halon-1211, based on an atmospheric lifetime of 10 years. Note the elevated mixing ratios for observed Halon-1211 since the mid-1990s compared to the latter predictions; if both the 10-year lifetime and the emissions from developed countries are correct, then these elevations would be the result of unreported emissions from developing countries and/or some unaccounted release from the large bank of Halon-1211 in developed countries. If the lifetime of Halon-1211 is significantly larger than 10 years, then emission estimates for all years are suspect. Data and model predictions are from Butler *et al.* (1998), updated for a lifetime of 10 years.

of estimates of emissions. As an example, Geller *et al.* (1997) use global measurements of SF<sub>6</sub> from the NOAA/CMDL Cooperative Network and selected ocean cruises, and from Maiss *et al.* (1996), together with a simple two-box atmospheric model to calculate emissions for 1996 of 5.9 ± 0.2 Gg SF<sub>6</sub> yr<sup>-1</sup>. This value is in agreement with estimates of industrial emissions made by Ko *et al.* (1993). Industrial production values (S&PS, 1997) are consistent with atmospheric observations (after

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accounting for banking) since 1972 and are estimated at  $7.6 \text{ Gg yr}^{-1}$  in 1996 (Maiss and Brenninkmeijer, 1998). From the Geller *et al.* (1997) global emission rate for 1996, it appears that a large fraction (approximately 80%) of  $\text{SF}_6$  produced each year is released from the stored bank and recent production into the atmosphere.

From the observed increase rates of the mixing ratios of atmospheric  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$ , annual global emissions of 15 to 18 Gg of  $\text{CF}_4$  (Harnisch *et al.*, 1996a) and  $1.9 \pm 0.15 \text{ Gg}$  of  $\text{C}_2\text{F}_6$  (Harnisch *et al.*, 1996a) have been inferred for 1994. Similarly, Zander *et al.* (1996c) estimated the amount of  $\text{CF}_4$  injected into the atmosphere at  $18 \pm 7 \text{ Gg}$  during 1994 based on the rate of increase determined from ATMOS observations in 1985 and 1994. Using data from an extensive survey on emissions carried out by the International Primary Aluminium Institute (IPAI) between 1990 and 1993 (IPAI, 1996), annual emissions of 12 to 17 Gg of  $\text{CF}_4$  and 1 to 2 Gg of  $\text{C}_2\text{F}_6$  can be calculated. Atmospheric accumulation and reported emissions thus agree reasonably well.

### 1.3.3 Chlorine Budget Estimates

#### 1.3.3.1 DISTRIBUTION OF ORGANIC CHLORINE ( $\text{CCl}_y$ )

Total  $\text{CCl}_y$  in the atmosphere is defined as the sum of the chlorine atoms bound in all organic chlorine-bearing source gases released to the atmosphere. This includes both natural and anthropogenic as well as short- and long-lived compounds. Based on the dominant Cl-bearing organic species,  $\text{CCl}_y$  can be evaluated according to

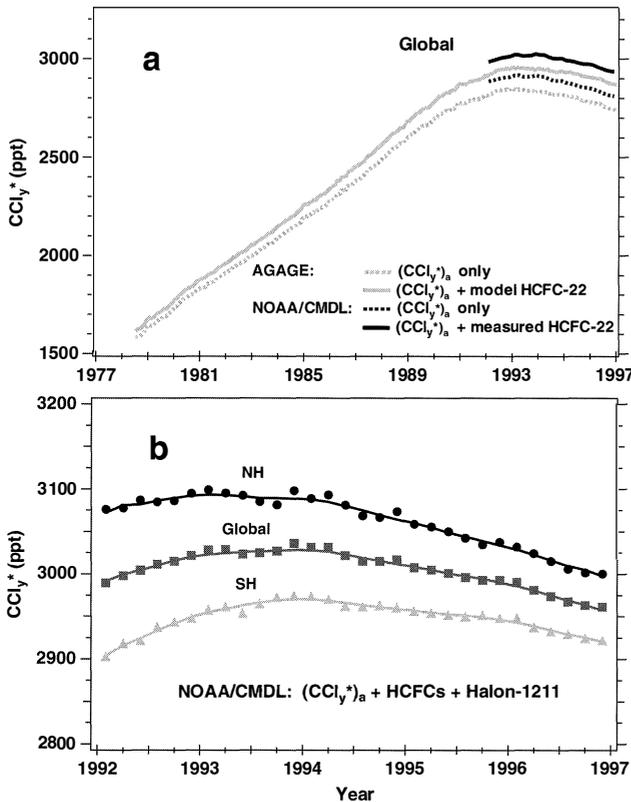
$$\begin{aligned} \text{CCl}_y = & 3[\text{CCl}_3\text{F}] + 2[\text{CCl}_2\text{F}_2] + 3[\text{CCl}_2\text{FCClF}_2] \\ & + 3[\text{CH}_3\text{CCl}_3] + 4[\text{CCl}_4] + [\text{CH}_3\text{Cl}] \\ & + [\text{CHClF}_2] + [\text{minor contributors}] \end{aligned} \quad (1-1)$$

where brackets indicate concentrations as dry mole fractions. Multipliers before the brackets indicate the number of chlorine atoms per molecule. Minor contributors (e.g.,  $\text{CClF}_3$ ,  $\text{CH}_2\text{Cl}_2$ , CFC-114, CFC-114a, CFC-115,  $\text{CHCl}_3$ ,  $\text{C}_2\text{Cl}_4$ , HCFC-141b, HCFC-142b, H-1211), which account for approximately 100 ppt (less than 3% of the total under all current circumstances), are neglected here.

None of the monitoring networks measures all species making up  $\text{CCl}_y$ , but two of them measure different but significant fractions,  $\text{CCl}_y^*$ , of the total  $\text{CCl}_y$  on a global basis. The ALE/GAGE/AGAGE network has estimated global  $\text{CCl}_y^*$  from CFC-11, -12, and -113,  $\text{CH}_3\text{CCl}_3$ , and  $\text{CCl}_4$  measurements since 1978, which is

labeled as  $(\text{CCl}_y^*)_a$  in Figure 1-14a (gray dotted line). Recently, ALE/GAGE/AGAGE has begun measuring HCFC-22 at SIO and Cape Grim, Tasmania, along with making measurements from archived flask samples containing air from Cape Grim. Including HCFC-22 global means generated from this dataset with a 2-D model, ALE/GAGE/AGAGE estimates the peak  $\text{CCl}_y^*$  at approximately 2950 ppt at some time between mid-1992 and mid-1994 (Figure 1-14a, gray solid line). Similar global estimates of the two different  $\text{CCl}_y^*$  sums (i.e., without and with HCFC-22) using NOAA/CMDL data are reproduced in Figure 1-14a as black dotted and solid lines, respectively. The offsets in  $\text{CCl}_y^*$  from the two networks represent small calibration differences. Tropospheric measurements of total  $\text{CCl}_y$  (Montzka *et al.*, 1996) from the NOAA/CMDL flask network (including both flask and in situ measurements for the CFCs,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CCl}_4$ , HCFC-141b, HCFC-142b, and Halon-1211) also show that the peak in  $\text{CCl}_y^*$  occurred sometime between mid-1992 and mid-1994 (Figure 1-14b) and was decreasing at a rate of  $25 \pm 5 \text{ ppt yr}^{-1}$  by mid-1995 (Montzka *et al.*, 1996). In both of these studies, explicit measurements of methyl chloride ( $\text{CH}_3\text{Cl}$ ) were not available for consideration. Because the presence of  $\text{CH}_3\text{Cl}$  in the atmosphere is believed to mostly result from natural processes (see Chapter 2), it was assumed that the  $\text{CH}_3\text{Cl}$  mixing ratio has remained constant during recent years; this assumption is supported by Khalil and Rasmussen (1998). When augmenting the data from Figure 1-14 with contributions from  $\text{CH}_3\text{Cl}$  and other minor species, it is estimated that the global peak  $\text{CCl}_y$  (as defined in Equation 1) occurred between mid-1992 and mid-1994, at a level equal to  $3700 \pm 100 \text{ ppt}$ . The subsequent  $\text{CCl}_y$  decline was primarily the result of the decrease observed in mixing ratios of  $\text{CH}_3\text{CCl}_3$  (Prinn *et al.*, 1995; Montzka *et al.*, 1996). Similar results for  $\text{CCl}_y$  have been obtained from the AGAGE measurements (Cunnold *et al.*, 1997).

One recent example of the detailed  $\text{CCl}_y$  determination in the stratosphere is based on measurements from the ATMOS instrument during the ATLAS-3 Space Shuttle mission in November 1994 (Zander *et al.*, 1996b). The source gases involved were CFC-11, CFC-12, HCFC-22,  $\text{CCl}_4$ , and  $\text{CH}_3\text{Cl}$ , all measured by ATMOS, complemented by  $\text{CH}_3\text{CCl}_3$  and CFC-113 derived from gas chromatographic analyses of flasks collected on a balloon platform, over southern France, one month before the ATLAS-3 mission; they are consistent with earlier stratospheric profile



**Figure 1-14.** (a) Different global mean estimates of tropospheric  $\text{CCl}_y^*$  from the ALE/GAGE/AGAGE and NOAA/CMDL networks. Dotted lines represent measured global means labeled  $(\text{CCl}_y^*)_a$  from the principal chlorocarbons CFC-11, -12, and -113,  $\text{CH}_3\text{CCl}_3$ , and  $\text{CCl}_4$ . Solid lines include HCFC-22 global mixing ratios. ALE/GAGE/AGAGE updated data available from Prinn *et al.* (1998). (b) Tropospheric  $\text{CCl}_y^*$  estimated on a bimonthly basis for the Northern Hemisphere (circles, NH), Southern Hemisphere (triangles, SH), and global (squares) from the halocarbons measured by the NOAA/CMDL flask network since early 1992 (updated from Montzka *et al.* (1996) in Elkins *et al.* (1998)). For total  $\text{CCl}_y$  as per Equation (1-1), add about 650 ppt to each line for the unmeasured species  $\text{CH}_3\text{Cl}$  and the relatively minor contributors listed in the text. Curves through data points represent a non-parametric least-squares fit, where the fractional weighting factor is 30% (Cleveland and Devlin 1988).

determinations (e.g., Zander *et al.*, 1992) and with tropospheric concentrations for the individual compounds involved.

### 1.3.3.2 DISTRIBUTION OF INORGANIC CHLORINE ( $\text{Cl}_y$ )

$\text{CCl}_y$  compounds (see Equation (1-1)) mix into the stratosphere and are broken apart by photolysis and reaction with OH and  $\text{O}(^1\text{D})$ , producing  $\text{Cl}_y$  bound in reactive and reservoir gases. The dominant species of reactive (with ozone)  $\text{Cl}_y$  are: chlorine monoxide ( $\text{ClO}$ ) and its dimer  $\text{ClOCl}$ , hypochlorous acid ( $\text{HOCl}$ ), and chlorofluorocarbonyl ( $\text{COCIF}$ ). The dominant reservoir species of  $\text{Cl}_y$  are  $\text{ClONO}_2$  and  $\text{HCl}$ . Total  $\text{Cl}_y$ , which includes the carbonyl compound  $\text{COCIF}$ , is equal to the sum of both reactive and nonreactive forms, i.e.,

$$\begin{aligned} \text{Cl}_y = & [\text{Cl}] + 2[\text{Cl}_2] + [\text{OCIO}] + [\text{ClO}] + 2[\text{ClOCl}] \\ & + [\text{HOCl}] + [\text{COCIF}] + [\text{HCl}] + [\text{ClONO}_2] \\ & + [\text{ClONO}] + [\text{BrCl}] \end{aligned} \quad (1-2)$$

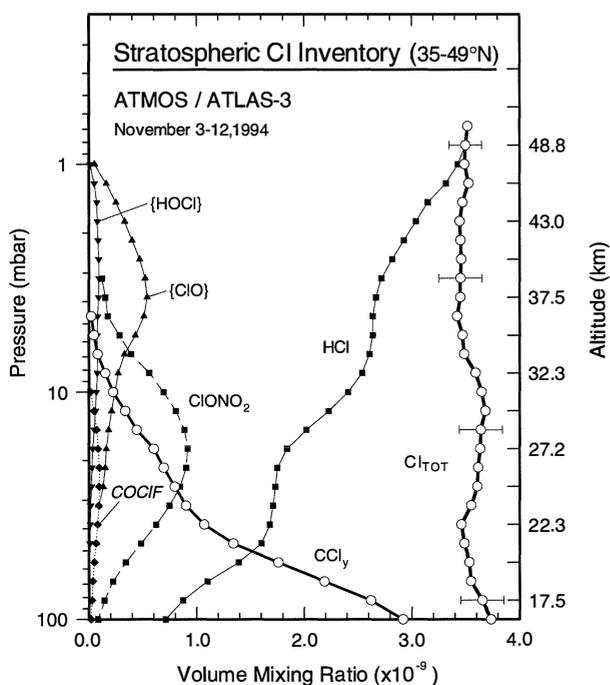
As a logical complement to the  $\text{CCl}_y$  evaluation discussed in Section 1.3.3.1, Zander *et al.* (1996b) combined the ATMOS/ATLAS-3 measurements of the inorganic species  $\text{HCl}$  and  $\text{ClONO}_2$  with mixing ratios of: (i)  $\text{ClO}$  obtained by the Millimeterwave Atmospheric Sounder (MAS) during ATLAS-3, (ii)  $\text{HOCl}$  obtained with the MkIV FTIR spectrometer during a balloon flight in September 1993 near  $32^\circ\text{N}$ , scaled by a 3% increase per year to represent the  $\text{HOCl}$  loading at the time of the ATLAS mission, and (iii)  $\text{COCIF}$  calculated by an atmospheric chemistry model.

The total chlorine  $\text{Cl}_{\text{TOT}}$  at the time of entry into the stratosphere, which includes the sum of  $\text{CCl}_y$  and  $\text{Cl}_y$ , is defined as

$$\text{Cl}_{\text{TOT}}(\text{entry}) = [\text{CCl}_y] + [\text{Cl}_y] \quad (1-3)$$

The resulting mean  $\text{Cl}_{\text{TOT}}$  between 16.5 and 50 km altitude was  $3.53 \pm 0.1$  ppb (1 standard deviation) during the ATLAS-3 mission; its observed partitioning, for the latitudinal zone  $35^\circ\text{N}$  to  $49^\circ\text{N}$ , is displayed in Figure 1-15. It should be noted here that, within the measurement uncertainties of typically  $\pm 5\%$ ,  $\text{Cl}_{\text{TOT}}$  is equal to  $\text{Cl}_y$  above 40 km altitude, as only trace amounts of  $\text{Cl}$ -bearing source gases persist at such heights. A difference of about 6% in  $\text{Cl}_{\text{TOT}}$  between the lower and upper stratospheric layers can be explained by invoking the lag time to mix  $\text{Cl}_{\text{TOT}}$  between these two levels (Zander *et al.*, 1996b).

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**Figure 1-15.** Mean vertical volume mixing ratio profiles of individual dominant species of  $\text{Cl}_y$ ,  $\text{CCl}_y$ , and total chlorine ( $\text{Cl}_{\text{TOT}}$ ) derived from the ATMOS/ATLAS-3 mission of November 1994 (Zander *et al.*, 1996b).  $\text{Cl}_{\text{TOT}}$  is the sum of  $\text{CCl}_y$ ,  $\text{HCl}$ ,  $\text{ClONO}_2$ ,  $\text{ClO}$ ,  $\text{HOCl}$ , and  $\text{COClF}$ .

### 1.3.3.3 CONSISTENCY AND TRENDS OF $\text{Cl}_y$ AND $\text{CCl}_y$

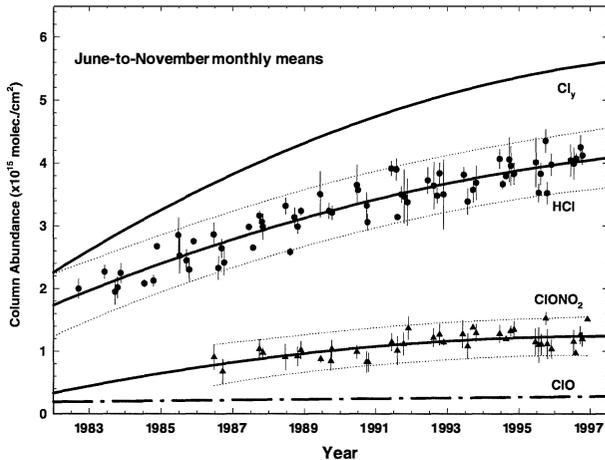
There is overall approximate consistency in chlorine atom inventories for the source, sink, and reservoir species. The resulting  $\text{Cl}_{\text{TOT}}$  is preserved throughout the stratosphere and is consistent with chlorine loading monitored at the ground, when accounting for a troposphere-to-middle-stratosphere mixing time of about five years (Zander *et al.*, 1996b; Chang *et al.*, 1996b).

In addition, after accounting for transport lags, the trends of  $\text{Cl}_y$  observed from ground- and space-based platforms are consistent with measurements of  $\text{CCl}_y$  in the troposphere.  $\text{HCl}$  and  $\text{ClONO}_2$ , which are the largest and longest-lived reservoirs of  $\text{Cl}_y$ , should show growth rates commensurate with total  $\text{CCl}_y$  trends in the troposphere, after accounting for the troposphere-stratosphere mixing time. Thus, a comparison of both forms of chlorine is possible under the assumption that this mixing time is known, i.e., 3 to 6.5 years depending on latitude and altitude (Russell *et al.*, 1996c; Volk *et*

*al.*, 1997; Harnisch, 1996). The column abundances above ISSJ of  $\text{HCl}$  from 1985 to 1995 (Zander *et al.*, 1996a) and of  $\text{ClONO}_2$  from 1986 to 1994 (Rinsland *et al.*, 1996b) showed mean trends of  $3.9 \pm 0.2\% \text{ yr}^{-1}$  and  $4.0 \pm 0.7\% \text{ yr}^{-1}$ , respectively. By combining these updated observational databases over the current overlapping period (Figure 1-16) and adding a  $\text{ClO}$  background loading derived from model calculations, it is found that the rate of increase of  $(\text{HCl} + \text{ClONO}_2 + \text{ClO})$  was equal to  $3.7 \pm 0.3\% \text{ yr}^{-1}$  from 1991 to 1993 and  $1.8 \pm 0.3\% \text{ yr}^{-1}$  from 1995 to 1997. The former value is comparable with the mean stratospheric  $3.3 \pm 0.2\% \text{ yr}^{-1}$  trend of  $\text{Cl}_{\text{TOT}}$  measured by ATMOS over the spring 1985 to fall 1994 time period (Zander *et al.*, 1996b), and all are consistent with the growth of  $\text{CCl}_y$  that prevailed during the mid- and late 1980s, i.e., between 3 and 4%  $\text{yr}^{-1}$  (WMO, 1990, 1992). The  $\text{ClONO}_2$  columns derived above the ISSJ are commensurate with those derived by Reisinger *et al.* (1994) over Lauder (45.0°S) between September 1990 and August 1994, but the latter show no statistically significant trend (i.e.,  $1.3 \pm 2\% \text{ yr}^{-1}$ ) over that four-year period.

An additional and independent confirmation of the consistency between total  $\text{Cl}_y$  and total  $\text{CCl}_y$  comes from the UARS HALOE experiment (Russell *et al.*, 1993). From a global series of  $\text{HCl}$  volume mixing ratios measured near 55 km altitude from October 1991 to April 1995 (see Section 1.2.8), and model evaluations of  $\text{Cl}$ -bearing compounds not fully converted into  $\text{HCl}$ , Russell *et al.* (1996c) derived a  $\text{Cl}_y$  rate of increase equal to  $(108 \pm 7) \text{ ppt yr}^{-1}$ , which translates into a trend of  $(3.7 \pm 0.3)\% \text{ yr}^{-1}$  referred to mid-1993, in good agreement with the above reported  $\text{Cl}_y$  increases. From comparisons with tropospheric  $\text{Cl}$ -bearing source gas inventories and model calculations, Russell *et al.* (1996c) concluded that all but a few percent (3 to 7%) of observed stratospheric chlorine amounts can be accounted for by known anthropogenic and natural tropospheric emissions, the former dominating the latter.

Recent in situ measurements of  $\text{CCl}_y$  from ACATS-IV (Elkins *et al.*, 1996b),  $\text{CCl}_y$  from whole air samples (Daniel *et al.*, 1996),  $\text{HCl}$  from Aircraft Laser Infrared Absorption Spectrometer (ALIAS) (Webster *et al.*, 1994, 1998), and  $\text{ClO}$  and  $\text{ClONO}_2$  from a new  $\text{Cl}_y$  instrument, aboard the NASA ER-2 aircraft during the Photochemistry of Ozone Loss in Arctic Region in Summer (POLARIS) mission from Fairbanks, Alaska, show that calculated  $\text{Cl}_y$  from  $(\text{Cl}_{\text{TOT}} - \text{CCl}_y)$  agrees with observed  $\text{Cl}_y$  at most altitudes within the experimental errors of



**Figure 1-16.** Evolution of the total inorganic  $\text{Cl}_y$  loading, based on HCl and  $\text{ClONO}_2$  monthly mean vertical column abundance determinations above the Jungfraujoch and a background ClO amount derived from model calculations. The observational databases are extensions of those reported by Zander *et al.* (1996a) for HCl and by Rinsland *et al.* (1996b) for  $\text{ClONO}_2$ . Only measurements made between June and November are included, to avoid significant column variability during winter and spring periods.

the measurements (Sen *et al.*, 1998).

The conclusion that can be made from the data discussed above is that there remains little doubt that the bulk of chlorine atoms in today's stratosphere and its temporal evolution are primarily associated with the release of anthropogenic chlorine-bearing gases at the Earth's surface.

### 1.3.4 Bromine Budget Estimates

#### 1.3.4.1 TRENDS OF ORGANIC BROMINE

Six gases contribute predominantly to the organic bromine budget in the troposphere, i.e., methylbromide ( $\text{CH}_3\text{Br}$ ), bromochloromethane ( $\text{CH}_2\text{BrCl}$ ), dibromomethane ( $\text{CH}_2\text{Br}_2$ ), and Halon-1211, -1301, and -2402. The total organic bromine mixing ratio,  $\text{CBr}_y$ , using only these dominant species, is defined as:

$$\text{CBr}_y = [\text{CH}_3\text{Br}] + [\text{CH}_2\text{BrCl}] + 2[\text{CH}_2\text{Br}_2] + [\text{CBrClF}_2] + [\text{CBrF}_3] + 2[\text{CBrF}_2\text{CBrF}_2] \quad (1-4)$$

where brackets indicate dry mixing ratios and multipliers before the brackets indicate the numbers of bromine atoms per molecule. Concentration measurements and rates of increase for the long-lived halons have been reviewed in Section 1.2.3 and summarized in Figure 1-4. The other shorter-lived compounds of Equation (1-4) are dealt with in Chapter 2. Total organic bromine measurements from whole air samples collected at the tropical tropopause in 1996 averaged  $17.4 \pm 0.9$  ppt (Schauffler *et al.*, 1998a); methyl bromide accounted for 55% of the total organic bromine, Halon-1301 for 13.6%, Halon-1211 for 19.8%, Halon-2402 for 5.1%,  $\text{CH}_2\text{Br}_2$  for 5.7%,  $\text{CH}_2\text{BrCl}$  for 0.7%, and  $\text{CHBrCl}_2$  for 0.1%. The resulting  $\text{CBr}_y$  shows a growth rate of about 2.2% per year, all from the halons (Butler *et al.*, 1998; Wamsley *et al.*, 1998).

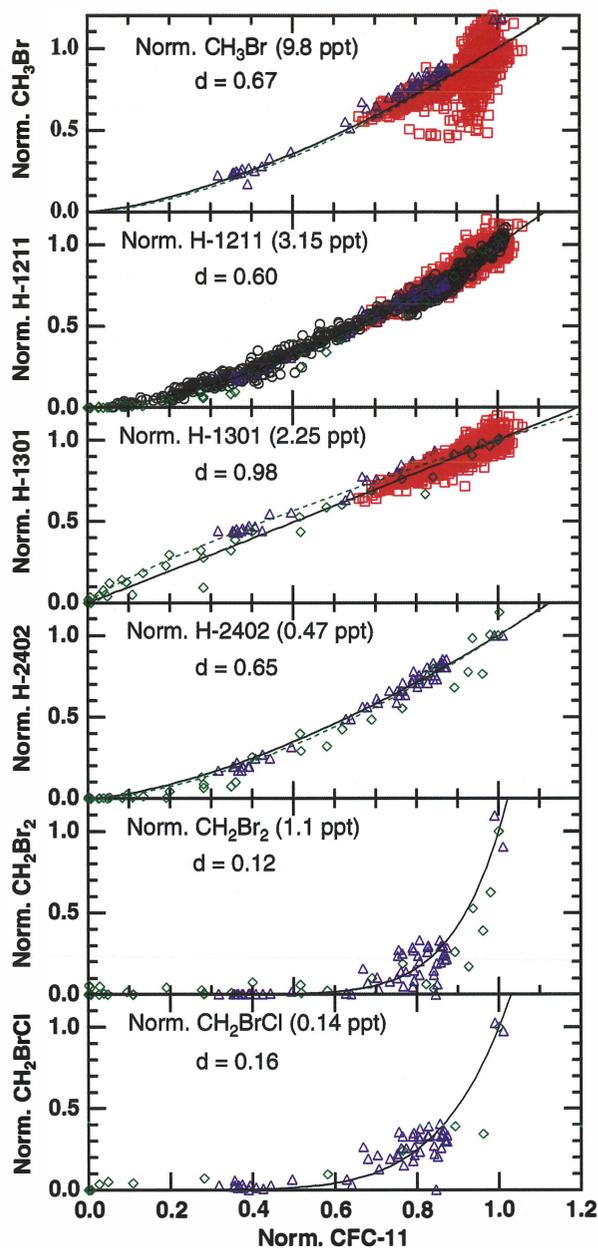
#### 1.3.4.2 ORGANIC BROMINE IN THE STRATOSPHERE

The correlation of the concentrations of organic bromine species with CFC-11 concentrations is very reproducible when normalized for the atmospheric growth of the species (Wamsley *et al.*, 1998). This normalization is required to compare datasets from different locations and times. The results from a number of aircraft and balloon measurements, and two-dimensional (2-D) model calculations (Weissenstein *et al.*, 1996) are consistent with each other (Figure 1-17). Additional aircraft measurements from whole air samples collected in 1996 (Schauffler *et al.*, 1998b) show consistent correlations with previous 1991 to 1992 measurements from whole air samples (Avallone and Prather, 1997). The correlation between two species with stratospheric mixing ratios that are represented by a stratospheric loss rate ( $1/\tau$ ) can be described by a power law relationship with a power coefficient equal to the ratios of the loss rates of the two species (Wamsley *et al.*, 1998). The correlations between the brominated species and CFC-11 are adequately described by a simple power law,

$$[\text{X}]/[\text{X}]_o = ([\text{CFC-11}]/[\text{CFC-11}]_o)^{1/d} \quad (1-5)$$

where the mixing ratio of each brominated species is represented by  $[\text{X}]$ , the subscript, o, designates the mid-October 1994 volume mixing ratio at the tropopause, and  $(1/d)$  is the power coefficient. Wamsley *et al.* (1998) were able to calculate  $\text{CBr}_y$  for each bromine species in Equation (1-4) using the measured values of Halon-1211

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and CFC-11 during the ASHOE/MAESA campaign of 1994, and the correlations of the unmeasured species with CFC-11 (Figure 1-17). Adding up the individual components from Equation (1-4), it is found that the correlation between  $CBr_y$  and CFC-11 is very good in the stratosphere (Figure 1-18a). The solid curve is the best fit to the correlation using Equation (1-5) with  $d = 0.58$ . The effective stratospheric lifetime of  $CBr_y$  in today's atmosphere is estimated to be approximately one half that of CFC-11.

**Figure 1-17.** Normalization datasets and resulting correlations for the six organic bromine species versus CFC-11 included in the calculation of organic bromine from Wamsley *et al.* (1998). The solid curves are the best fits to the data using Equation (1-5). The October 1994 surface mixing ratio for each molecule is given in parentheses. ACATS-IV data are shown in black circles (Elkins *et al.*, 1996b), National Center for Atmospheric Research (NCAR) data in blue triangles (Schauffler *et al.*, 1993), University of East Anglia (UEA) data in green diamonds, and University of California-Irvine in red squares (Blake *et al.*, 1992). The dashed curves are fits to the Atmospheric and Environmental Research, Inc. (AER) model results (Weissenstein *et al.*, 1996) matched for season and location with the NCAR data. The value of  $d$  for the modeled Halon-1211 correlation is 0.60, which makes it difficult to distinguish from the measured correlation (0.53).

### 1.3.4.3 INORGANIC BROMINE ( $Br_y$ ) IN THE STRATOSPHERE

Measurements of  $Br_y$  species in the stratosphere are extremely difficult because of their low volume mixing ratios and high reactivity to surfaces. Total  $Br_y$  is composed of the following:

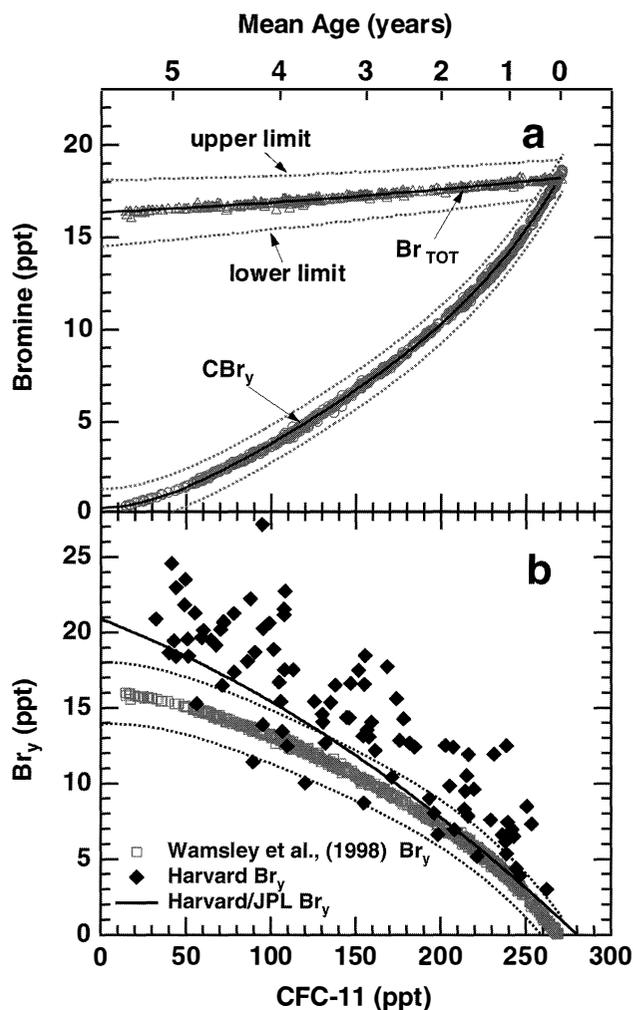
$$Br_y = [Br] + [BrO] + 2[Br_2] + [BrONO] + [BrCl] + [BrONO_2] + [HOBr] + [HBr] \quad (1-6)$$

where the factor before the bracket indicates the number of bromine atoms per molecule and the brackets indicate the dry volume mixing ratio of the compound. A recent study (Lary, 1996) found that the lifetimes of  $Br_2$ ,  $BrONO$ ,  $BrCl$ ,  $BrONO_2$ , and  $HOBr$  are less than one day in sunlight at 20 km altitude. For typical midlatitude conditions, model calculations show that the volume mixing ratio of  $Br_y$  is about 2 times the value of  $BrO$  (Salawitch *et al.*, 1994).

$Br_y$  can be calculated indirectly using the total organic bromine,  $CBr_y$  from Equation (1-4), and the observed tropospheric trends for total bromine ( $Br_{TOT}$ ) at the time of entry into the stratosphere at the tropical tropopause, from the relation

$$Br_{TOT}(\text{entry}) = [Br_y] + [CBr_y] \quad (1-7)$$

and solving for  $Br_y$  (Daniel *et al.*, 1996).



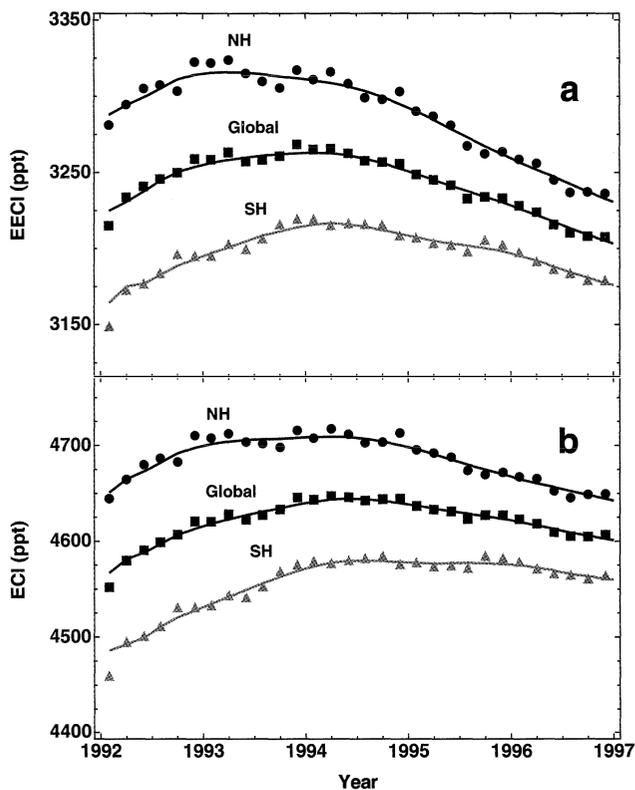
**Figure 1-18.** (a) Calculated results for  $Br_{TOT}$  (triangles) as a function of CFC-11, using the age of the air mass from  $SF_6$  observations, reported trends for the atmospheric halons (Butler *et al.*, 1998), and the sum of all organic bromine compounds,  $CBr_y$  (circles) for each observation during ASHOE/MAESA (Wamsley *et al.*, 1998). (b) Calculated mixing ratios of  $Br_y$  as a function of CFC-11, using the Wamsley *et al.* (1998)  $Br_y$  estimates from (a), and an earlier result labeled Harvard/JPL  $Br_y$ , derived from AASE II measurements (Salawitch *et al.*, 1994). The diamonds represent Harvard  $Br_y$  calculated using in situ  $BrO$  measurements during ASHOE/MAESA and  $Br_y$  partitioning from a photochemical model. The dashed curves represent upper and lower limits within one-standard-deviation windows including all measurement uncertainties for bromine estimates by Wamsley *et al.* (1998).

During the ASHOE/MAESA mission in 1994, concurrent measurements were made of Halon-1211 by NOAA/CMDL and  $BrO$  by Harvard (Wamsley *et al.*, 1998). From these measurements,  $Br_y$  was calculated using the indirect organic bromine method (Wamsley *et al.* (1998)  $Br_y$  in Figure 1-18b) and an indirect  $Br_y$  method based on  $BrO$  and other species measurements (Harvard  $Br_y$  in Figure 1-18b). A fit to earlier organic bromine measurements by the whole air sampler (WAS) instrument during AASE II in 1992 is included for comparison (Harvard/Jet Propulsion Laboratory (JPL)  $Br_y$  in Figure 1-18b; Salawitch *et al.*, 1994). The value of the Harvard  $Br_y$  in the oldest air parcels (lowest CFC-11) is 20 (+11, -9.8) ppt. This value is higher than the Wamsley *et al.* (1998)  $Br_y$ , but within the experimental errors of each approach. The differences between the two methods could be explained if  $Br_y$  from the troposphere is transported to the stratosphere, as suggested by Ko *et al.* (1997), or if there is some missing compound in the calculation of organic bromine ( $CBr_y$  as per Equation (1-4)), or if the  $Br_y$  partitioning is in error (Wamsley *et al.*, 1998). Lower values of  $BrO$  (by 30%) were measured using the same  $BrO$  instrument discussed in Wamsley *et al.* (1998) but were based on an earlier airborne mission in 1991 to 1992 and a different instrument calibration (Avallone *et al.*, 1995). If these lower values of  $BrO$  are correct, then the calculated  $Br_y$  would be in better agreement with the Wamsley *et al.* (1998)  $Br_y$  estimates in Figure 1-18b. The Harvard/JPL  $Br_y$  calculated by Salawitch *et al.* (1994) did not include a later calibration scale change of the WAS results (Daniel *et al.*, 1996), which would improve the agreement between the Wamsley *et al.* (1998)  $Br_y$  and the Harvard/JPL  $Br_y$ . If the lower Wamsley *et al.* (1998)  $Br_y$  mixing ratios are confirmed, then there could be 20% less calculated  $BrO$  abundance and consequently, 20% less calculated ozone loss resulting from bromine chemistry in old air, relative to previous estimates.

### 1.3.5 Total Equivalent Chlorine Evaluation

Although amounts of organic Cl in the troposphere have started declining, Br from halons is still increasing. In order to estimate how the future abundance of stratospheric ozone will respond to these changes, the trends for both Cl- and Br-containing compounds must be considered. This is especially true, despite the low concentrations observed for atmospheric Br, because on a per-atom basis, Br has an inordinately large influence upon stratospheric ozone concentrations when compared

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**Figure 1-19.** Amounts of Cl and Br in the NH (circles), SH (triangles) and global (squares) troposphere, expressed as effective equivalent chlorine (EECl; frame a) and as equivalent chlorine (ECl; frame b) that are predicted to be released (at some future time) from the halocarbons shown in Figure 1-14b, as inorganic halogen, respectively in the lower midlatitude stratosphere (EECl) and in the springtime, polar stratospheric vortex (ECl). Both EECl and ECl are calculated using  $\alpha = 60$ . Curves through data points represent a nonparametric least-squares fit where the fractional weighting factor is 30% (Cleveland and Devlin, 1988). Predictions are updates from Montzka *et al.* (1996), with all data available in Elkins *et al.* (1998).

to Cl. The relative impact of bromine compared to chlorine at destroying stratospheric ozone is characterized by a parameter called  $\alpha$  (e.g., Solomon *et al.*, 1992). Whereas bromine atoms may be about 40 times more effective than chlorine atoms in destroying stratospheric ozone in the polar vortex, they may be as much as 100 times more efficient in the lower midlatitude stratosphere (Daniel *et al.*, 1995; Montzka *et al.*, 1996). The values of  $\alpha$  remain highly uncertain, and a mean value of approximately 60 is being adopted when dealing with globally averaged ozone losses (see Section 11.4.1 of Chapter 11). By weighting tropospheric mixing ratios according to their relative decomposition rates for individual compounds within the different regions, it is possible to use tropospheric measurements to predict how mixing ratios of inorganic halogens will affect stratospheric ozone in the future. Estimates of the future abundances of reactive halogen compounds for the lower midlatitude stratosphere (effective equivalent chlorine, EECl) and for the springtime polar stratosphere (equivalent chlorine, ECl) are made with halogen release rates for each region and  $\alpha = 60$  (Figure 1-19). Note that EECl is similar to the equivalent

effective stratospheric chlorine (EESC) described in Chapter 11, but does not explicitly include a delay of three years for transport from the troposphere to the stratosphere (Daniel *et al.*, 1995). Compounds not measured but included in Figure 1-19, such as  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CClF}_3$ ,  $\text{CH}_2\text{Cl}_2$ , CFC-114 and -115,  $\text{CHCl}_3$  and  $\text{CCl}_2\text{CCl}_2$ , contribute about 990 ppt to EECl and about 1300 ppt to ECl. After these inclusions, the estimate for ECl (Figure 1-19b) is an upper limit for the amount of reactive halogen available to participate in the ozone-depleting reactions in the polar regions. The mean global tropospheric burden of organic halogen that will become inorganic halogen in the future midlatitude stratosphere reached a maximum between 1993 and 1994 and was declining afterwards at  $-22 \pm 2$  ppt EECl  $\text{yr}^{-1}$  (updated from Montzka *et al.* (1996), with  $\alpha = 60$ ). By comparison, the tropospheric burden of halogen predicted in the future polar stratosphere peaked in late 1993 and early 1994, and was decreasing afterwards at  $-18 \pm 3$  ppt ECl  $\text{yr}^{-1}$  (updated from Montzka *et al.* (1996), with  $\alpha = 60$ ). The small growth rate of  $\text{CH}_3\text{Br}$  and the contribution from the unaccounted species are not expected to significantly change these results.

### 1.3.6 Fluorine Budget Estimates

Measurements of atmospheric fluorine, which does not affect stratospheric ozone, provide us with an independent check on the anthropogenic contribution to stratospheric chlorine loading by CFCs, because CFCs are also the predominant sources of inorganic fluorine-bearing compounds in the stratosphere. Total inorganic fluorine ( $F_y$ ), which includes the carbonyl compounds  $\text{COF}_2$  and  $\text{COCIF}$ , is defined as:

$$F_y = [\text{HF}] + 2[\text{COF}_2] + [\text{COCIF}] \quad (1-8)$$

HF and  $\text{COF}_2$  contribute 98% of the total  $F_y$  column (Zander *et al.*, 1992) and 92% or more of the  $F_y$  vertical profile when considering altitude distributions (Sen *et al.*, 1996). The combination of vertical column abundance measurements of HF and  $\text{COF}_2$  (Mélen *et al.*, 1998) made at the ISSJ between 1985 and 1997, indicates that  $F_y$  increased at a mean rate of  $4.8 \pm 0.3\% \text{ yr}^{-1}$  for the period 1985 to 1997 (Zander *et al.*, 1996a). Recent space-based investigations of the inorganic fluorine budget of the stratosphere have been made with ATMOS and HALOE. While the ATMOS measurements of HF and  $\text{COF}_2$  in 1985 and 1992 led to stratospheric  $F_y$  rates of change equal to  $73 \pm 5 \text{ ppt yr}^{-1}$  (Zander *et al.*, 1994c; Gunson *et al.*, 1994), surrogates of  $F_y$  deduced from HF measurements by HALOE near the stratopause were  $85 \pm 2 \text{ ppt yr}^{-1}$  for the period November 1991 to April 1995 (Russell *et al.*, 1996c). These values are commensurate with the tropospheric organic fluorine ( $\text{CF}_y$ ) rates of change measured during the 1980s, i.e.,  $75 \pm 13 \text{ ppt yr}^{-1}$ , which result primarily from changes in CFC releases. Including the results for chlorine (Section 1.3.3.3), this agreement between the two total fluorine estimates strengthens the conclusion that the CFCs are responsible for most of the stratospheric loading of both inorganic fluorine and chlorine, as well as for the ozone depletion by the latter.

The midlatitude fluorine abundance reported for September 1993 by Sen *et al.* (1996) indicates a steady decrease of total fluorine with increasing altitude, from a tropospheric value of about 1.82 ppb to 1.48 ppb at 38 km altitude. The latter value, made up entirely of the reservoir species, is commensurate with tropospheric concentrations of fluorine reported in the late 1980s, with time-dependent 2-D model predictions (1.45 ppb), and with the fluorine budget derived from the ATMOS/ATLAS-1 Space Shuttle flight in 1992 (Zander *et al.*, 1994c).

### 1.3.7 Budgets Based on Model Assimilations

As discussed later, the observed mole fractions can be used to constrain sources and sinks (Section 1.4.3). Deduction of emissions is possible using a global chemical transport model in which sources are adjusted using optimal inverse methods until a satisfactory fit to observed concentrations is obtained (Prinn and Hartley, 1995; Hartley and Prinn, 1993).

These methods have been applied to determine global emissions of  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_4$ , and  $\text{CCl}_2\text{FCClF}_2$  for comparison with industry estimates (Cunnold *et al.*, 1997; Simmonds *et al.*, 1998; Fraser *et al.*, 1996). Considering the uncertainty in industry estimates introduced by end-use and nonreporting-company uncertainties, the agreement between the inverse and industry estimates is satisfactory for  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  but not for  $\text{CCl}_2\text{FCClF}_2$ . Possible reasons for the latter discrepancy are discussed in Fraser *et al.* (1996).

Inverse methods have also been applied to determine regional emissions (Hartley and Prinn, 1993; Hartley *et al.*, 1994, 1996; Haas-Laursen *et al.*, 1996; Mulquiney *et al.*, 1998). From studies of  $\text{CCl}_3\text{F}$ , whose regional emissions are quite well known, it is apparent that transport processes predicted in climate models are not accurate enough to be used in the estimation of regional emissions. Climate models, for example, do not simulate the El Niño-Southern Oscillation (ENSO), which clearly affects SH trace gas concentrations (Prinn *et al.*, 1992; Elkins *et al.*, 1993). The use of transport models based on observed winds shows promise but there are still significant discrepancies between industry and inverse-method estimates of regional  $\text{CCl}_3\text{F}$  emissions (Mahowald *et al.*, 1997). These discrepancies could result from inadequate treatment of transport or from insufficient spatial density in the current observing networks (Hartley *et al.*, 1996).

## 1.4 LIFETIMES

### 1.4.1 Introduction

This section examines the lifetimes of species discussed in this chapter. The atmospheric abundance of a trace gas that is released at the Earth's surface and removed by photochemical reactions in the atmosphere is governed by the equation

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$$\frac{dB(t)}{dt} = E(t) - \int L n dV \quad (1-9)$$

where  $B(t)$  is the burden defined by  $\int n dV$ ;  $n(x,y,z,t)$  is the local number density of the gas;  $E(t) = \int E(x,y,z=0,t) dx dy$  is the emission rate at the surface; the in situ removal rate is given by  $L n$  where  $L(x,y,z,t)$  is the loss frequency;  $t$  is the time coordinate;  $dV = dx dy dz$ ;  $x, y, z$  are the Cartesian coordinates along the longitudinal, latitudinal, and vertical directions, respectively; and the integral is over the whole atmosphere. The loss frequency could be generalized to include washout and deposition at the ground. In this chapter, we will limit our discussion to in situ photochemical removal.

Equation (1-9) can be written in the form

$$\frac{dB(t)}{dt} = E(t) - \frac{B(t)}{\tau(t)} \quad (1-10)$$

where  $\tau(t)$  is the instantaneous lifetime defined by the atmospheric burden divided by the atmospheric removal rate:

$$\tau(t) = \frac{\int n dV}{\int L n dV} \quad (1-11)$$

For trace gases with lifetimes of a few years or longer, it is more appropriate to look at the annually averaged versions of Equations (1-10) and (1-11), which are denoted by adding brackets  $\langle \rangle$  around the relevant variables and replacing  $t$  by  $T$ , where  $T$  represents time variations on the interannual time scale.

The lifetime  $\langle \tau \rangle (T)$  can be computed from the annually averaged Equation (1-11) using the distributions of  $L$  and  $n$  determined either from observations or model computation. One advantage for model computation is that one can compute lifetimes for species that are not yet emitted to the atmosphere. This will be the subject for Section 1.4.2.1. Alternatively, for species whose burden is proportional to the surface concentrations, the annually averaged Equation (1-10) can be used to derive  $\langle \tau \rangle (T)$  from the time series of observed surface concentrations and known emission rates using statistical techniques without referring to specific details about  $L$  and  $n$ . This method of deriving lifetime will be discussed in Section 1.4.3.

### 1.4.2 Lifetimes from Stratospheric Distributions and Stratospheric Removal Rates

Here we discuss the determination of lifetimes using  $L$  and  $n$  either from model calculations or observations. It is useful to distinguish between instantaneous lifetimes and steady-state lifetimes. Instantaneous lifetimes correspond to the values from the annually averaged Equation (1-10) where values of  $n$  and  $L$  in the current atmosphere are used. Steady-state lifetimes correspond to the special situation where the species is in steady state and  $\frac{d \langle B \rangle (T)}{dT}$  is zero.

The instantaneous lifetime can be different from the steady-state lifetime as it depends on the emission history of the gas and the changes in the chemical composition of the atmosphere. Current estimates indicate that there is a delay of about 2 to 4 years in transporting material from the troposphere to the lower/middle stratosphere (see Chapter 8, WMO, 1992; Schmidt and Khedim, 1991; Pollock *et al.*, 1992; Woodbridge *et al.*, 1995; Daniel *et al.*, 1996; Boering *et al.*, 1996; Volk *et al.*, 1997). For a species whose burden is increasing (decreasing) with time, the concentration in the stratospheric sink region is systematically smaller (larger) than would be obtained at steady-state, when the emission is balanced by stratospheric removal. Thus, the instantaneous lifetime of the species is longer (shorter) than the steady-state lifetime if the burden is increasing (decreasing) with time.

#### 1.4.2.1 LIFETIMES FROM MODEL-CALCULATED STRATOSPHERIC DISTRIBUTION AND STRATOSPHERIC REMOVAL

##### *Model Results*

A numerical model simulating transport and removal of trace gases can be used to compute  $L$  and  $n$ . These simulations require the use of appropriate boundary conditions. The boundary values could be constant in time to simulate a steady state, or they can be time-dependent to simulate the temporal evolution in the atmosphere. For either case, model-calculated  $L$  and  $n$  for any particular species can be used in Equation (1-10) to calculate  $\langle \tau \rangle (T)$ . If a time-dependent boundary condition is used in the calculation, this lifetime is the instantaneous lifetime. A steady-state lifetime can be obtained from Equation (1-10) where  $n$  is the steady-

**Table 1-4. Model-calculated steady-state lifetimes in years.**

Species	AER <sup>a</sup>	GSFC <sup>a</sup>	CSIRO <sup>a</sup>	Harvard 2-D <sup>a</sup>	LLNL <sup>a</sup>	SUNY -SPB <sup>a</sup>	UNIVAQ 2-D <sup>a</sup>	LaRC 3-D <sup>a</sup>	GISS-UCI 3-D <sup>b</sup>	MIT 3-D <sup>c</sup>
N <sub>2</sub> O	109	130	117	122	106	125	122	175	113	124
CCl <sub>3</sub> F (CFC-11)	47	61	53	68	49	49	44	57	35	42
CCl <sub>2</sub> F <sub>2</sub> (CFC-12)	92	111	100	106	92	107	105	149	90	107
CCl <sub>2</sub> FCClF <sub>2</sub> (CFC-113)	77	101	83	55	81	87	81	-	70	79
CCl <sub>4</sub>	41	53	46	64	42	39	36	42	28	30
CBrClF <sub>2</sub> (H-1211)	16 <sup>d</sup>	12 <sup>e</sup>	36 <sup>f</sup>	-	-	-	21 <sup>f</sup>	29 <sup>f</sup>	21	-
CBrF <sub>3</sub> (H-1301)	63	78	69	-	-	-	61	93	52	-

<sup>a</sup> Results are taken from the Model and Measurement Workshop II (M&M II) (Park *et al.*, 1998). The models and the contact persons are as follows: AER - Atmospheric and Environmental Research, Inc., U.S., Malcolm Ko; GSFC - NASA Goddard Space Flight Center, U.S., Charles Jackman; CSIRO - Commonwealth Scientific and Industrial Research Organisation (CSIRO) Telecommunications and Industrial Physics, Australia, Keith Ryan; Harvard 2-D - Harvard University, U.S., Hans Schneider; LLNL - Lawrence Livermore National Laboratory, U.S., Doug Kinnison; SUNY-SPB - State University of New York at Stony Brook, U.S., Marvin Geller; UNIVAQ 2-D - University of L'Aquila, Italy, Giovanni Pitari; LaRC 3-D - NASA Langley Research Center, U.S., William Grose. LaRC is the only 3-D model that participated in M&M II.

<sup>b</sup> Results given are for steady-state lifetimes from Avallone and Prather (1997). The values should be close to the atmospheric lifetimes except for Halon-1211.

<sup>c</sup> Results for MIT model from Table 5-2 of Kaye *et al.* (1994). MIT model described in Golombek and Prinn (1993) and references therein.

<sup>d</sup> Calculated using cross section from Burkholder *et al.* (1991).

<sup>e</sup> Calculated using cross section from DeMore *et al.* (1987).

<sup>f</sup> Calculated using the Halon-1211 cross section from DeMore *et al.* (1997) that did not give any recommendation beyond 288 nm.

state distribution calculated assuming  $E$  is constant in time and  $L$  is calculated assuming fixed (time invariant) boundary conditions for all trace gases.

Table 1-4 gives the calculated steady-state lifetimes from several models. The differences in the lifetimes can be attributed to differences in both photochemistry and transport in the models. Equation (1-11) states that  $1/\langle\tau\rangle$  is the average of  $L$  weighted by  $n$ . The species distribution is determined by the local balance between transport and  $L$ . The removal rate,  $L$ , also depends on transport because transport can affect the calculated ozone in the model that drives the photolysis rates. Thus, to resolve the difference, one would have to compare the model-computed ozone with the observed ozone. Next, we discuss how observations can be used to resolve some of these differences.

### ***Reducing Uncertainties by Comparison with Observations***

For the purpose of validating the model-calculated lifetimes, we use comparisons of  $L$  and  $n$  in the lower stratosphere where the product  $Ln$  contributes to the bulk of the integrated removal rate.

Several components that enter into the model calculation of photolysis rates contribute to the uncertainties in the computed lifetime. The photolysis rate ( $J$ ) of a species is the sum of the product of the local solar flux, absorption cross section, and quantum yield of the species at each wavelength. The solar flux at a particular location in the atmosphere is determined by attenuation of the solar flux by the overhead O<sub>2</sub> and O<sub>3</sub> columns. The unattenuated solar flux,  $F$ , is uncertain by

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about 5% and varies as a function of wavelength with cyclical solar activity. It is difficult to use in situ measurements of local solar UV flux to validate  $F$  because small uncertainties in the  $O_2$  and  $O_3$  columns can translate into large changes in  $J$  for large optical depth. Further coordination with the measurement programs such as those reported in Herman and Mentall (1982), Anderson and Hall (1986), and McElroy (1995) is needed for future validation. Uncertainties in the absorption cross section and quantum yield of the species will also translate into uncertainties for the calculated photolysis rate. However, because all models used the same photolysis rates (DeMore *et al.*, 1997), it would not explain the spread in the model results shown in Table 1-4. Finally, questions can be raised about the algorithms that are used in the models to compute the photolysis rates. Many of the models have participated in an intercomparison of the photolysis rates in 1995. In that exercise, the algorithm for computing  $J$  was tested by comparing the computed  $J$  in the models to that computed by a detailed radiative transfer code. Many models have modified their algorithms to get good agreement. For some models that participated in the intercomparison exercise (Atmospheric and Environmental Research, Inc. (AER), Goddard Space Flight Center (GSFC), Lawrence Livermore National Laboratory (LLNL)), it is reasonably certain that any difference in photolysis rate is due to differences in the ozone distribution computed by each model.

Transport is uncertain because both the strength of the resolved circulation (vertical and horizontal winds) and the magnitude of the eddy diffusion (vertical and horizontal) are uncertain. Model transport can be tested by comparing model-computed distributions of long-lived tracers such as  $N_2O$  and CFCs with observations. However, this is complicated by the uncertainties in the removal rates of these gases. An alternative is to use a photochemically inert tracer such as the radioactive tracer  $^{14}C$ , which is produced from galactic cosmic rays and nuclear explosions (Johnston, 1989; Shia *et al.*, 1989; Kinnison *et al.*, 1994). Unfortunately, this test is not sensitive to the transport parameters in the lower stratosphere. A more fundamental issue in the comparison of model results (which represent climatological mean conditions) with observations involves the large variabilities in the observed concentrations at any location caused by the short-term

vertical and horizontal displacements of air during passages of synoptic-scale disturbances. Thus, one can never be certain whether any particular measurement is representative of the climatological mean condition at that location. Several techniques have been developed to facilitate model-observation comparisons. Some studies (e.g., Schoeberl *et al.*, 1989; Lait *et al.*, 1990) showed that observations taken at different locations and times can be compared more readily if they are collated using potential temperature and potential vorticity instead of altitude and latitude. Hartmann *et al.* (1989) pointed out that if one displays the observed species concentrations against the concentration of  $N_2O$  of the same air mass in a correlation diagram, the results from different locations show an almost linear correlation with  $N_2O$ . This feature can be exploited as discussed in the next section.

In addition, it is possible to extract information from observations to compare with transport parameters for the lower stratosphere in 2-D models. Several studies (Minschwaner *et al.*, 1996; Volk *et al.*, 1996; Schoeberl *et al.*, 1997) derived a replacement time constant of 10 to 18 months for air in the lower tropical stratosphere from mixing of midlatitude air. Shia *et al.* (1998) showed that this can be related to the value of the horizontal diffusion coefficient  $K_{yy}$  used in the model and that a  $K_{yy}$  value of  $7 \times 10^4 \text{ m}^2 \text{ sec}^{-1}$  is appropriate for the tropical lower stratosphere. The observed ratio of  $NO_y/O_3$  (Fahey *et al.*, 1996) also provides a constraint for the combination of advection and eddy mixing in the lower stratosphere. Weisenstein *et al.* (1996) showed that a value for  $K_{yy}$  of  $3 \times 10^4 \text{ m}^2 \text{ sec}^{-1}$  in the tropics best reproduces the results in the AER model. However, the interpretation is made more difficult because of the uncertainties in the  $NO_2$  and ozone budgets in the upper troposphere. In the AER model, steady-state lifetimes calculated using the smaller  $K_{yy}$  ( $3 \times 10^4 \text{ m}^2 \text{ sec}^{-1}$ ) are about 10% shorter than the values given in Table 1-4 (calculated using  $7 \times 10^4 \text{ m}^2 \text{ sec}^{-1}$ ). Other methods for validating the combined effects of advection and eddy mixing include comparing the model-computed age of air (Hall and Plumb, 1994) with that derived from observation of  $SF_6$  (Volk *et al.*, 1997). Given these uncertainties, it is difficult to use direct comparison of  $n$  and  $L$  from model and observation to constrain the model-calculated lifetime to better than 30%.

### 1.4.2.2 INSTANTANEOUS LIFETIME FROM OBSERVATIONS

Johnston *et al.* (1979) used concentrations of N<sub>2</sub>O from balloon profiles along with model-calculated  $L$  to estimate the lifetime of N<sub>2</sub>O. Ko *et al.* (1991) used satellite-measured concentrations from Stratospheric and Mesospheric Sounder (SAMS) in their analysis and demonstrated that using the observed N<sub>2</sub>O distributions from different years could cause a change of about 15% in calculated lifetime. Recent satellite measurement programs have provided more data to construct  $n(x,y,z,t)$  for ozone and certain species. The distributions ( $n(x,y,z,t)$ ) for these species can be used along with photochemical loss rates ( $L(x,y,z,t)$ ) computed using the observed distribution of ozone to compute the lifetimes for these gases via Equation (1-11). Minschwaner *et al.* (1998) used observed concentrations of CFC-12 and N<sub>2</sub>O in the stratosphere from the Cryogenic Limb Array Etalon Spectrometer (CLAES) instrument on the Upper Atmosphere Research Satellite (UARS) to determine the global destruction rates and instantaneous lifetimes for these gases. Photolysis rates are calculated using the unattenuated solar UV irradiances measured from the Solar Stellar Irradiance Comparison Experiment (SOLSTICE) instrument on UARS and a line-by-line model of absorption in the Schumann-Runge bands. The computed instantaneous lifetimes based on the observed concentrations between March 1992 and January 1993 are  $114 \pm 22$  years for CFC-12 and  $118 \pm 25$  years for N<sub>2</sub>O. The uncertainties are estimates based on the standard deviation of the CLAES measurements in the midtropical stratosphere, uncertainties in the solar flux measurements and atmospheric transmission, and uncertainties in absorption cross sections of CFC-12 and N<sub>2</sub>O. The instantaneous lifetimes can be used to obtain a steady-state lifetime by assuming a mean age of air in the tropical midstratosphere, and a growth rate for the gas. After adjusting for the growth rate, Minschwaner *et al.* (1998) reported estimates for the steady-state lifetimes of  $103 \pm 25$  years for CFC-12 and  $117 \pm 26$  years for N<sub>2</sub>O.

As a modeling exercise for the “Models and Measurements Workshop II” (Park *et al.*, 1998) monthly averaged fields for N<sub>2</sub>O, CFC-12, and ozone were constructed from the UARS data and the GSFC model output. Five groups participated in computing the

lifetimes using these fields. The range for the computed lifetimes is typically 10% above and below the mean among the five models. This suggests that different ways of calculating photolysis rates and mapping of data into the model grid introduce an uncertainty of this magnitude in lifetimes.

### 1.4.2.3 STRATOSPHERIC LIFETIMES FROM OBSERVED TRACER CORRELATIONS AND TROPOSPHERIC GROWTH RATE

The theoretical work of Plumb and Ko (1992) provides an independent method for the semiempirical derivation of tracer lifetimes from stratospheric observations without the need to accurately describe stratospheric transport or chemistry. These authors investigated a conceptual “global mixing” model of the stratosphere, in which horizontal mixing everywhere dominates vertical advection. In this case mixing ratios of sufficiently long-lived tracers are globally homogenized along the same quasi-horizontal mixing surfaces such that their surfaces of constant mixing ratio coincide. This implies that the stratospheric abundances of two sufficiently long-lived tracers are uniquely correlated with each other, even as they fluctuate in time and space. Plumb and Ko (1992) also showed that in the “global mixing” model, stratospheric transport can be described by a one-dimensional flux-gradient relation. If the mixing ratios of two long-lived tracers,  $\sigma_1$  and  $\sigma_2$ , are in steady state, then the slope of their correlation in the lowermost stratosphere (below the regions where chemical sinks act) equals the ratio of their stratospheric removal rates and thus

$$\frac{\tau_1}{\tau_2} \equiv \frac{d\sigma_2}{d\sigma_1} \frac{B_1}{B_2} \quad (1-12)$$

where  $B_i$  is the total atmospheric burden for species  $i$  (as defined in Section 1.4.1), and  $\tau_i$  is its steady-state stratospheric lifetime, equal to the steady-state atmospheric lifetime for species without tropospheric sinks. Studies have demonstrated that Equation (1-12) is valid for model-generated lifetimes and slopes of the correlation diagrams from a 2-D model (Plumb and Ko, 1992) and a 3-D model (Avallone and Prather, 1997).

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Recent research has shown that the simple “global mixing” picture is violated in the tropics where horizontal mixing is not fast compared to vertical advection (Volk *et al.*, 1996; Hall and Waugh, 1997; Schoeberl *et al.*, 1997). As a consequence, stratospheric tracer interrelations are observed to differ between the tropics and midlatitudes (Volk *et al.*, 1996) or between the two hemispheres (Keim *et al.*, 1997). Plumb (1996) investigated the implications of a “tropical pipe” model, i.e., completely excluding horizontal mixing into the tropical region, and concluded that Equation (1-12) still applies provided that (i) the two tracers are tightly correlated in each hemisphere in the extratropical lower stratosphere, (ii) the interhemispheric difference of the extratropical correlation slope is small, and (iii) the correlation slope in Equation (1-12) is evaluated at the extratropical tropopause and from data taken during the winter half year that dominates net transport. Volk *et al.* (1997) argued that the same conclusions apply in the more realistic case of slow horizontal mixing into the tropics. An analysis of a comprehensive set of tracer observations from the 1994 ASHOE/MAESA ER-2 campaign shows that the above conditions for Equation (1-12) are indeed met (Volk *et al.*, 1997).

Volk *et al.* (1997) showed that, under the same conditions, steady-state stratospheric lifetimes may be derived from the gradient of the steady-state tracer mixing ratio,  $\sigma_i$ , with respect to the mean age of stratospheric air (Hall and Plumb, 1994),  $\Gamma$ , in the measured air parcels:

$$\frac{B_i}{\tau_i} = -\frac{d\sigma_i}{d\Gamma} N_u \quad (1-13)$$

where  $B_i$  is again the atmospheric burden of the respective species,  $N_u$  is the total number of molecules above the tropopause, and the gradient with respect to age,  $d\sigma_i/d\Gamma$ , needs to be evaluated exactly at the extratropical tropopause.

The variable  $\tau_i$  in Equations (1-12) and (1-13) corresponds to a steady-state lifetime only when the tracers are in steady state in the atmosphere. Thus, they cannot be easily used to obtain steady-state lifetimes of species that are not in steady state in the present-day atmosphere. If the tropospheric concentration of the species is changing with time, part of the tracer gradient at the tropopause is due to accumulation in the stratosphere and  $1/\tau_i$  in either equation has to be replaced

with  $\tau_i^{-1} + B'_u/B_i$  where  $\tau_i$  is the instantaneous lifetime and  $B'_u$  is the total accumulation rate of  $i$  above the tropopause, a quantity not easily assessed unless tropospheric growth has been linear for a long time and is accurately known. Volk *et al.* (1997) proposed an alternative method of accounting for tropospheric growth and non-steady-state mixing ratios,  $\chi_i$ , to obtain steady-state lifetimes. In the method, one deduces the correction factors  $C_i$  for each species using the following information:

- the tracer gradient with respect to age at the tropopause, observed  $d\chi_i/d\Gamma$ ;
- the time series of tropospheric mixing ratios of the respective species during a 5-year period prior to the stratospheric observations; and
- estimates of the width of the stratospheric age spectrum (Hall and Plumb, 1994) from 3-D transport models.

The steady-state gradient,  $d\sigma_i/d\Gamma$ , defined as (observed  $d\chi_i/d\Gamma$ )  $\cdot C_i$  is used in Equation (1-13) to obtain the steady-state lifetime. Volk *et al.* (1997) also showed that corrected steady-state correlation slopes defined as

$$\frac{d\sigma_i}{d\sigma_{\text{CFC-11}}} = \frac{d\chi_i}{d\chi_{\text{CFC-11}}} \frac{C_i}{C_{\text{CFC-11}}} \quad (1-14)$$

can be used in Equation (1-12) to derive steady-state lifetimes based on a given CFC-11 lifetime (CFC-11 is best suited as a reference tracer as its lifetime is known most accurately from the method discussed in Section 1.4.3).

Table 1-5 shows steady-state stratospheric lifetimes derived from ASHOE/MAESA observations by Volk *et al.* (1997). The stratospheric lifetimes listed in Table 1-5 equal atmospheric lifetimes with the exception of Halon-1211, because the other species are removed predominantly in the stratosphere. Results shown are obtained using two approaches: via Equation (1-12) using the corrected correlations of tracers with CFC-11 and an assumed CFC-11 lifetime of  $45 \pm 7$  years; and via Equation (1-13) whereby the age of stratospheric air was calculated from in situ observations of SF<sub>6</sub>. The correction factors ( $C_i$ ) for tropospheric growth and non-steady state  $\chi$  are also given. Note that these correction factors are time dependent and valid only for October 1994.

**Table 1-5. Stratospheric steady-state lifetimes (from Volk *et al.*, 1997).**

Species	Observed $d\chi_i/d\Gamma$ from ASHOE/MAESA (ppt yr <sup>-1</sup> , ±%)	Steady-state lifetime based on corrected gradient with respect to age (years ± years)	$d\chi_i/d\chi_{\text{CFC-11}}$ observed correlation slope relative to CFC-11 from ASHOE/MAESA (ppt/ppt, ± %)	Steady-state lifetime based on corrected correlation slope and $\tau_{\text{CFC-11}} = 45$ ± 7 years (years ± years)	Correction factor for tropospheric growth $C_i$
N <sub>2</sub> O	-13,000 ± 38%	124 ± 49	436 ± 11%	122 ± 22	0.97 ± 0.02
CCl <sub>3</sub> F (CFC-11)	-33.5 ± 28%	41 ± 12		(45 ± 7)	0.96 ± 0.02
CCl <sub>2</sub> F <sub>2</sub> (CFC-12)	-43.8 ± 25%	77 ± 26	1.29 ± 7%	87 ± 17	0.77 ± 0.07
CCl <sub>2</sub> FCClF <sub>2</sub> (CFC-113)	-7.3 ± 22%	89 ± 35	0.212 ± 20%	100 ± 32	0.65 ± 0.12
CCl <sub>4</sub>	-15.9 ± 32%	32 ± 11	0.515 ± 3.6%	32 ± 6	1.03 ± 0.02
CBrClF <sub>2</sub> (H-1211)	-0.84 ± 31%	20 ± 9	0.0237 ± 7%	24 ± 6	0.90 ± 0.10

Besides the uncertainty of the growth correction in the case of rapidly growing species, the main limitation of these methods lies in the determination of the correlation slope at the tropopause. The ASHOE/MAESA observations show that most correlations exhibit significant curvature toward the tropopause, presumably due to tropospheric growth and/or changes in the tracer fluxes across the tropical/midlatitude boundary. Highly resolved measurements in the vicinity of the tropopause are thus required to accurately measure the slope at the tropopause. With the data presently available, lifetimes based on the correlation with CFC-11 can be constrained to within about 20% (cf. Table 1-5), assuming that the lifetime of CFC-11 is known to within 15%.

#### 1.4.3 Lifetimes Estimated from Global Tropospheric Measurements of Trace Gases

The observed mole fraction ( $\chi$ ) of a species at a given time and location can be expressed as a line integral of the Lagrangian form of the continuity equation over a back-trajectory in space (or, equivalently, time). The integrand includes the net chemical production ( $Y$ ) of the species, defined as the difference between true chemical production and true chemical loss. Determination of  $Y$  is a classical inverse problem (Prinn and Hartley, 1995). It requires accurate definition of initial conditions and atmospheric circulation, and with these, an estimate of  $Y$  produces an estimate ( $\chi_e$ ) of the

mole fraction. Let  $E$  be the vector of errors (random with zero mean and uncorrelated in time) in the observable  $\chi$  at a network of observing stations. Hence the difference between observed and estimated mole fractions is

$$\chi - \chi_e = E - \Delta\chi_e \quad (1-15)$$

where  $\Delta\chi_e$  is the vector of errors in  $\chi_e$  caused by the error ( $\Delta Y$ ) in the previous estimate of  $Y$ . Now  $Y$  is formally a continuous function of space and time, but can be approximated by appropriate regional averages contained in a vector. The quasi-linear relation between the vector  $\Delta\chi_e$  and the vector of  $\Delta Y$  values is computed in a global chemical transport model to provide a so-called “partial derivative matrix.”

Fundamentally, we can only determine the net production ( $Y$ ) from the measurements. Hence, to interpret, say, surface measurements in terms of surface emissions as discussed in Section 1.3.7, we need to know the true chemical destruction rates (or equivalently, lifetimes). Alternatively, if we wish to determine lifetimes we must be given the surface emissions. To solve the inverse problem (i.e., determine the vector of  $Y$  values given the observed time series of  $\chi$  values at each station), it is common to use an optimal linear recursive least squares filter of the Kalman-type (Gelb, 1974; Cunnold and Prinn, 1991; Prinn and Hartley, 1995). This approach enables inclusion of measurement errors,  $E$ , and an objective estimate of the uncertainty in

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**Table 1-6. Equilibrium atmospheric lifetimes (years) estimated from ALE/GAGE/AGAGE measurements.** The tabulated values are based on the trend and inventory estimates; the values are similar to those reported in Cunnold *et al.* (1997) but they are for a slightly different time period.

Species	Inverse Lifetime (years <sup>-1</sup> )	Lifetime (years)	Observation Period Utilized
CCl <sub>3</sub> F (CFC-11)	0.019 ± 0.0059	52 (-12, +24)	July 1978 - June 1993
CCl <sub>2</sub> F <sub>2</sub> (CFC-12)	0.0054 ± 0.0041	185 (-80, +584)	July 1978 - June 1993

estimated  $Y$  values (related to the variance in the time series of corrections  $\Delta Y$  made to the previous estimates of  $Y$ ). In this way, the atmospheric lifetimes of long-lived gases, for which the atmospheric releases are well-quantified, may be estimated from the atmospheric inventory of these gases and from long-term trends in the atmospheric concentrations over periods of five or more years. Estimates of the lifetimes of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> (Cunnold *et al.*, 1994) and CH<sub>3</sub>CCl<sub>3</sub> (Prinn *et al.*, 1995) have thus been reported.

The inventory estimates of the lifetimes for the CFCs have been obtained by comparing measured concentrations (from the ALE/GAGE/AGAGE) against predicted values. Differences between measured and predicted values are minimized over a specified time period (e.g., 1978 to 1993) and in essence, the lifetimes by the inventory technique represent average estimates over the period. During times when CFCs are increasing in the atmosphere, the stratospheric content lags behind the tropospheric content because of the several-year time lag associated with the time for CFCs released at the ground to reach the stratosphere. The atmospheric lifetime is therefore time-dependent; consequently the lifetimes reported here refer to an equilibrium period (similar to that for CCl<sub>3</sub>F currently) when the releases at the surface exactly equal the global losses in the stratosphere. The uncertainties in the lifetime estimates by the inventory technique for the CFCs consist of absolute calibration uncertainties of approximately 1%, uncertainties in the representativeness of four or five ground-based sites, combined with the use of a 2-D model to infer the atmospheric content (approximately 3%) (Cunnold *et al.*, 1994) and uncertainties in release. Although the historical record of production figures for companies that report to AFEAS is believed to be very accurate (approximately 1%), uncertainties of

approximately 3% in the annual release figures are associated with estimates of the time lag between production and release (Fisher and Midgley, 1994). Moreover, the production and release uncertainties were larger for the nonreporting companies such as those in Russia, China, and India. This situation has improved with the availability of UNEP data.

Atmospheric lifetimes are also estimated from the trends in the measured concentrations. The ability of the ALE/GAGE/AGAGE network to maintain a constant calibration over the 17-year period is most important for this estimation. This has been validated by comparisons against recent measurements of archived air samples from the entire 17-year period. The release uncertainties described in the previous paragraph dominate the uncertainties in the lifetime estimates from the trend technique.

The lifetimes of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> are given in Table 1-6. Lifetime estimates by the inventory technique from any sub-period within this 15-year period are similar. There is some tendency for the trend lifetime estimate to change with time but the change is well within the stated error bars. Because of the long lifetimes, the estimates are equally as sensitive to the uncertainties in release in the early 1970s as they are to the releases in 1992. Starting from 1992, the chemical industry has no longer attempted to include estimates of releases by non-reporting countries in their estimates of world production and release. Moreover, both industry practices and atmospheric observations suggest that there could have been changes in the delay between production and release of the CFCs since 1992 (Cunnold *et al.*, 1997). Therefore the lifetime estimates are based on the mid-1978 to mid-1993 period only.

The ALE/GAGE/AGAGE measurements of CCl<sub>2</sub>FCClF<sub>2</sub> should have provided good estimates of its

**Table 1-7. Comparison of reference steady-state lifetimes from WMO (1995) with model-calculated ranges and lifetimes derived from observations.** All lifetimes are in years.

Species	Reference Lifetimes from WMO [1995] <sup>a</sup>	Model Range <sup>b</sup>	Volk SF <sub>6</sub> <sup>c</sup>	Volk CFC-11 <sup>d</sup>	Minschwaner UARS <sup>g</sup>	AGAGE <sup>e</sup>
N <sub>2</sub> O	120	106-175	124 ± 49	135 ± 16	117 ± 26	
CCl <sub>3</sub> F (CFC-11)	50	35-68	41 ± 12	50 <sup>d</sup>		52 (40-76)
CCl <sub>2</sub> F <sub>2</sub> (CFC-12)	102	90-149	77 ± 26	96 ± 12	103 ± 25	185 (105-769)
CCl <sub>2</sub> FCClF <sub>2</sub> (CFC-113)	85	55-101	89 ± 35	112 ± 31		
CCl <sub>4</sub>	42	28-64	32 ± 11	36 ± 4		
CBrClF <sub>2</sub> (H-1211)	20	12-36	20 ± 9 <sup>f</sup>	26 ± 5 <sup>f</sup>		
CBrF <sub>3</sub> (H-1301)	65	61-93				

<sup>a</sup> From Table 13-1, WMO (1995).<sup>b</sup> From Table 1-4.<sup>c</sup> Derived steady-state stratospheric lifetimes based on gradient with age derived from SF<sub>6</sub> data; from Volk *et al.* (1997).<sup>d</sup> Derived steady-state stratospheric lifetimes based on gradient with CFC-11 and an adopted lifetime of 50 years for CFC-11; from WMO (1995). Compare to values based on 45 years from Table 1-5.<sup>e</sup> From Table 1-6. The range is calculated using the uncertainty in the inverse lifetime given in the table.<sup>f</sup> Because Halon-1211 is dissociated by photolysis in the longwave, there is significant removal in the troposphere so that the stratospheric lifetimes should not be compared directly to the global lifetime. See text for further discussion.<sup>g</sup> Steady-state lifetime from Minschwaner *et al.* (1998) derived using UARS observations, assumed mean age, and tropospheric growth rates.

lifetime using procedures similar to those used for CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub>. Unfortunately the emissions inferred from the atmospheric measurements are approximately 10% smaller than the estimates by industry (Fraser *et al.*, 1996). This difference is similar in magnitude to the estimates of the emissions by the nonreporting companies (AFEAS, 1998). This disagreement results in lifetime estimates of approximately 26 years by the inventory technique and greater than 100 years by the trend technique (Fraser *et al.*, 1996). This spread has narrowed somewhat with the addition of two more years of measurements but the lifetime estimates currently only indicate that the results are not inconsistent with stratospheric photodissociation being the only sink for CCl<sub>2</sub>FCClF<sub>2</sub>.

#### 1.4.4 Reference Steady-State Lifetimes

The previous Assessment report (WMO, 1995) gave a set of reference steady-state lifetimes for use in calculations of the Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs) of the species. The same reference lifetimes were also used as response times in halogen loading calculations. These values (from Table 13-1 of WMO (1995)) are listed in Table 1-7. Given the new information in this chapter, particularly the new formalism (Volk *et al.*, 1997) that enables us to derive steady-state lifetimes from stratospheric measurements, we conclude that the WMO (1995) reference lifetimes for some gases need revision.

With the exception of CFC-11, the WMO (1995) reference lifetimes for the species listed are the mean

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values from model results of several groups reported in Kaye *et al.* (1994). This method is clearly unsatisfactory in the present context because there are no well-established criteria on which model results listed in Table 1-4 should be included in taking the average. It is more useful to examine how the model-computed lifetimes have changed as the models have evolved. As discussed in Section 1.4.2.3, several 2-D models have modified the transport parameters in the models to simulate the effect of a tropical barrier. Results from the AER model show that restricting the mixing through the barrier leads to shorter calculated lifetimes (Shia *et al.*, 1998). A second observation is that the lifetimes for CFC-11 and CCl<sub>4</sub> from two of the three 3-D models are much shorter than those calculated by the 2-D models (see Table 1-4). It could be argued that lifetimes calculated by 3-D models may be more realistic because they have a more direct (i.e., 3-D) representation of the transport processes in the atmosphere. However, more work is needed to assure that the vertical resolution in such models is sufficient to resolve the scale heights of the species with short local lifetimes.

The Volk *et al.* (1997) formalism provides, for the first time, a way to obtain steady-state stratospheric lifetimes from observations. With the exception of Halon-1211, the species listed in Table 1-7 have very little removal in the troposphere. As a result, the derived stratospheric lifetimes can be compared directly to atmospheric lifetimes. As is evident in Table 1-7, the derived lifetimes for CFC-11, CCl<sub>4</sub>, and CFC-12 are in the shorter end of the model range, and shorter than the WMO (1995) reference lifetimes. It is also interesting to note that the derived shorter lifetimes are in better agreement with the lifetimes calculated by two of the three 3-D models in Table 1-4. The large uncertainties in the derived lifetimes given in column 4 of Table 1-7 arise from the uncertainty in the SF<sub>6</sub> measurement from the 1994 ASHOE/MAESA campaign. The uncertainty has been reduced in subsequent flights. The lifetimes relative to CFC-11 derived by Volk *et al.* (1997) have much smaller uncertainties because  $d\sigma_i/d\sigma_{\text{CFC-11}}$  can be determined more accurately. When referenced to a CFC-11 lifetime of either 45 years (Table 1-5, column 5) or 50 years (Table 1-7, column 5), with the exception of CCl<sub>4</sub> and Halon-1211, these derived lifetimes agree within their uncertainties with the WMO (1995) reference lifetimes.

Because CFC-11 is used as the reference gas in the definition of the Ozone Depletion Potential, extra

care was used in selecting its WMO (1995) reference value, basing it on observations as well as model calculations. The WMO (1995) value of 50 years is in good agreement with the central estimate of the lifetime from ALE/GAGE/AGAGE measurements (Cunnold *et al.*, 1997), but not with the central estimate of 41 years by Volk *et al.* (1997). The derived lifetime range for CFC-11 using the Volk *et al.* (1997) method (29 to 53 years) just includes the value of 50 years. However, a new reference value between 41 and 50 years would lie well within the ranges of both the Cunnold *et al.* (1997) and Volk *et al.* (1997) estimates.

Butler *et al.* (1998) showed that the observed burden of Halon-1211 is inconsistent with the emissions if one uses the H-1211 reference lifetime of 20 years. Because of disagreement between the measurements of Gillotay and Simon (1989) and Burkholder *et al.* (1991) for the absorption cross sections for wavelengths longer than 288 nm, the Jet Propulsion Laboratory Data Evaluation Panel did not give any recommended values for these wavelengths (DeMore *et al.*, 1997). Burkholder *et al.* (1991) estimated the partial lifetime due to photolysis in the long-wavelength region to be about 20 years. If one combines this with the derived stratospheric lifetime of 24 years (Table 1-5, column 5), the atmospheric lifetime should be about 11 years. The WMO (1995) reference lifetime of 20 years was again obtained by averaging the model results from Kaye *et al.* (1994). It is likely that some models ignored the longwave photolysis in their calculations and biased the average toward the longer lifetimes.

Based on the above discussion, we recommend new reference lifetimes for three gases. The new reference lifetime for CFC-11 of 45 years lies between the central estimates of Volk *et al.* (1997) and Cunnold *et al.* (1997) (Tables 1-5 and 1-6), provides the same estimated CCl<sub>4</sub> lifetime by the two Volk *et al.* (1997) methods (Table 1-5), and gives an estimate of the atmospheric lifetime for H-1211 of 11 years, in better agreement with observations of its atmospheric burden (Butler *et al.*, 1998). The new reference lifetime for CCl<sub>4</sub> of 35 years lies just above the central estimates of Volk *et al.* (1997), but at the low end of the model range (Table 1-4). We have also rounded the reference lifetime of CFC-12 to 100 years, to better reflect its uncertainty. These new reference lifetimes were reported earlier in Table 1-1 of the scientific summary of this chapter. Note that some calculations in later chapters were carried out before these WMO 1998 values were finalized and hence

used WMO 1995 values instead. While a more comprehensive analysis is required, adoption of the above CFC-11, Halon-1211, and  $\text{CCl}_4$  lifetimes as reference values is an appropriate response to knowledge gained since the WMO (1995) Assessment.

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## Appendix

### Ground-Based Stations and Their Geographic Coordinates

Station	Latitude	Longitude	Elevation (m)	Network(s) <sup>1</sup>
Adrigole, Ireland	52°N	10°W	50	AGAGE
Alert, North West Territories, Canada	82.45°N	62.52°W	210	CMDL, UH
Cape Grim, Tasmania, Australia	40.41°S	144.64°E	94	AGAGE, CMDL
Cape Kumukahi, Hawaii, U.S.	19.52°N	154.82°W	3	CMDL
Cape Meares, Oregon, U.S.	45.48°N	123.97°W	10	AGAGE
Fraserdale, Canada	49.88°N	81.57°W	210	UH
Izana, Tenerife	28.33°N	16.48°W	2376	UH
Jungfrauoch, Switzerland	46.5°N	8.0°E	3580	NDSC
Kitt Peak, Arizona, U.S.	31.9°N	111.6°W	2090	NDSC
Lauder, New Zealand	45.0°S	169.7°E	370	NDSC
Mace Head, Ireland	53.33°N	9.90°W	16	AGAGE
Mauna Loa, Hawaii, U.S.	19.54°N	155.58°W	3397	CMDL, NDSC
Neumayer, Antarctica	71.6°S	8.3°W	16	UH
Niwot Ridge, Colorado, U.S.	40.04°N	105.54°W	3013	CMDL
Ragged Point, Barbados	13.17°N	59.02°W	34	AGAGE
Scripps Pier, California, U.S.	32.83°N	117.27°W	14	AGAGE
South Pole, Antarctica	89.98°S	102.00°E	2841	CMDL
Table Mountain, California, U.S.	34.4°N	117.7°W	2258	NDSC
Trinidad Head, California, U.S.	41.05°N	124.15°W	109	AGAGE
Tuluila, American Samoa	14.23°S	170.56°W	77	CMDL, AGAGE
WITN tower, North Carolina, U.S.	35.37°N	77.39°W	9	CMDL

<sup>1</sup> Advanced Global Atmospheric Gases Experiment (AGAGE); NOAA Climate Monitoring and Diagnostics Laboratory (CMDL); Network for the Detection of Stratospheric Change (NDSC); University of Heidelberg (UH).