

CHAPTER 1

Controlled Substances and Other Source Gases

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CHAPTER 1

CONTROLLED SUBSTANCES AND OTHER SOURCE GASES

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SCIENTIFIC SUMMARY

- As a result of the Montreal Protocol and its Amendments and Adjustments, organic chlorine in the global troposphere continues to decline slowly, and inorganic chlorine in the global stratosphere has stabilized.
 - (a) Total organic chlorine from long- and short-lived chlorocarbons continues to decline in the global troposphere. Total tropospheric chlorine in 2000 was about 5% lower than observed at its peak (3.7 ± 0.1 parts per billion (ppb)) in 1992-1994, and the rate of change in 2000 was about -22 parts per trillion per year (ppt yr^{-1}) ($-0.6\% \text{ yr}^{-1}$). The influence of methyl chloroform on this decline is diminishing. Total organic chlorine from chlorofluorocarbons (CFCs) is no longer increasing at Earth's surface.
 - (b) Total inorganic chlorine in the atmosphere, as estimated from hydrogen chloride and chlorine nitrate total column absorbance measurements, stopped increasing in 1997-1998 and has remained fairly constant since. Because most atmospheric hydrogen chloride and chlorine nitrate reside in the stratosphere, this result provides an estimate of chlorine changes in the stratosphere. These stratospheric changes are consistent with expectations based on our understanding of trace gas trends in the troposphere, stratospheric chemistry, and atmospheric mixing processes.
 - (c) Space-based measurements show that the global mean growth rate of hydrogen chloride at 55 km has been substantially less since 1997 than it was before that time. Although the measurements since 1997 also show short-term variations, the recent data do not show the steady increases observed in the early 1990s.
- Recent results from observations of tropospheric and stratosphere bromine show the following:
 - (a) As of 2000, total organic bromine from halons continued to increase in the troposphere at about $0.2 \text{ ppt Br yr}^{-1}$ ($\text{pmol mol}^{-1} \text{ yr}^{-1}$), and halons accounted for nearly 8 ppt of bromine. Global trend data for methyl bromide, a gas that is responsible for about half of the 20 ppt of total bromine in today's stratosphere, have not been updated since the previous Assessment. Atmospheric histories inferred from Southern Hemisphere air archives and Antarctic firn air suggest that, assuming similar changes in both hemispheres, total organic bromine from the sum of methyl bromide and halons has more than doubled since the mid-1990s.
 - (b) Measurements of inorganic bromine in the stratosphere indicate a rate of increase consistent with observed tropospheric trends of halons and methyl bromide, but mixing ratios that are 4-6 ppt higher. Additional stratospheric bromine stems from the transport of nonanthropogenic, very short-lived gases (such as bromoform and dibromomethane) and their degradation products to the stratosphere.
- Ozone-depleting halogens in the troposphere, as assessed by calculating chlorine equivalents from measurements of organic chlorine- and bromine-containing source gases, continue to decrease. As of mid-2000, equivalent organic chlorine in the troposphere was nearly 5% below the peak value in 1992-1994. The recent rate of decrease is slightly less than in the mid-1990s owing to the reduced influence of methyl chloroform on this decline.
- Trends of ozone-depleting substances in the atmosphere have been updated, and 20th century trends have been deduced from air trapped in snow above glaciers (firn air).
 - (a) In 2000, tropospheric mixing ratios of CFC-11 and -113 were decreasing faster than in 1996, and mixing ratios of CFC-12 were still increasing, but more slowly.
 - (b) Global methyl chloroform mixing ratios have been declining exponentially since 1998 because of the rapid drop in emissions to low levels; mixing ratios in 2000 were less than one-half of the peak observed in 1992. As a result, the rate of decline observed for methyl chloroform (and chlorine from methyl chloroform) during 2000 was about two-thirds of what it was in 1996.
 - (c) Newly reported measurements of air from firn allow inferences regarding 20th century histories of ozone-depleting substances in the atmosphere. These data confirm that nonanthropogenic sources of chlorofluorocarbons, halons, carbon tetrachloride, methyl chloroform, and hydrochlorofluorocarbons are insignificant. They are consistent, however, with there being substantial natural emissions of both methyl chloride and methyl bromide.

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- Atmospheric halocarbon measurements can provide some assessment of past global compliance with production restrictions in the Montreal Protocol, and these considerations provide the foundation for projecting halocarbon mixing ratios in future scenarios.
 - (a) The substantial reductions in emissions of ozone-depleting substances during the 1990s that are inferred from measured atmospheric trends are consistent with controls on production and consumption in the fully amended and adjusted Montreal Protocol. Consumption in developing countries is now a significant contributor to global emissions. The year 1999 is the first in which production and consumption of a class of ozone-depleting substances (the CFCs) were restricted in all Parties to the Montreal Protocol. Atmospheric measurements are consistent with emissions derived from reported global production data for CFCs.
 - (b) The updated, best-estimate scenario (Ab) for future halocarbon mixing ratios suggests that the atmospheric burden of halogens will return to the 1980, pre-Antarctic-ozone-hole levels around the middle of this century, provided continued adherence to the fully amended and adjusted Montreal Protocol. Only small improvements would arise from reduced production allowances in the future. Lack of compliance to the Protocol controls would delay or prevent recovery of stratospheric ozone.
- With respect to hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), the gases used as interim substitutes for CFCs, halons, and chlorinated solvents, this Assessment found the following:
 - (a) Organic chlorine from the HCFCs in the troposphere reached nearly 180 ppt in 2000 and represented 6% of total chlorine from anthropogenic gases. The rate of increase in organic chlorine from HCFCs remained constant at about 10 ppt yr⁻¹ from 1996 to 2000.
 - (b) Discrepancies reported in past Assessments between atmospheric observations and expectations based on industry-reported production and emissions have narrowed substantially for HCFC-142b. This improvement stems from a better description of the functions relating emissions to usage in foam applications.
 - (c) Mixing ratios of HFC-134a and -23 have continued to increase in recent years, and by 2000 each had approached about 15 ppt in the background atmosphere. Three additional HFCs (HFC-125, -124, and -152a) have been identified in the remote troposphere, but their abundance in 2000 was low (1-3 ppt).
- New lifetime recommendations are made in this Assessment:
 - (a) The global lifetime of carbon tetrachloride is estimated to be 26 years, or about 25% shorter than in the previous Assessment. This shorter lifetime stems from identification of an ocean sink that is inferred from widespread observations of carbon tetrachloride undersaturation in surface waters of the ocean. Emissions inferred from this shorter lifetime and measured trends in 1996 are about a factor of 2 larger than those estimated from industry production data for that year. This apparent discrepancy, however, is within the rather large uncertainties in both estimates. Emissions inferred from atmospheric measurements and a lifetime of 26 years are about 7 times greater than the limits to global production set for 2005.
 - (b) In this Assessment, the global lifetime of Halon-1211 is taken to be 16 years based upon the mid-range of modeling results. This lifetime estimate and estimates of emission magnitudes and atmospheric mixing ratios contain substantial uncertainties. Observational studies and emission histories have not reduced the uncertainties in the global lifetime of 9-25 years calculated in models.
 - (c) The lifetime of methyl chloroform has been revised from 4.8 to 5.0 years based upon new observations. The implications of this change on our estimates of atmospheric hydroxyl suggest slightly longer lifetimes for HCFCs, HFCs, methane, and all other gases removed from the atmosphere by this important oxidant.
- With respect to methyl bromide and methyl chloride, ozone-depleting gases with both natural and human-derived sources, this Assessment found the following:
 - (a) A substantial imbalance remains in estimates of source and sink magnitudes for both methyl bromide and methyl chloride; known sinks outweigh sources for both of these gases. New sources of methyl bromide from individual crops and ecosystems have been identified, and new sources of methyl chloride from tropical plants have been discovered. These findings have narrowed the budget imbalances for both of these gases. Additional studies continue to show that the ocean is a small (10-20 Gg yr⁻¹) net sink for atmospheric methyl bromide,

although this results from a balance of large production and loss terms. Our understanding of the saturation of methyl bromide in ocean waters has been refined, but the estimates of net flux between the ocean and atmosphere remain essentially unchanged.

- (b) Twentieth-century trends of methyl bromide and methyl chloride have been inferred for the Southern Hemisphere from analyses of firn air. Provided these gases are neither produced nor destroyed in the firn, these trends suggest 20th century increases in the Southern Hemisphere of about 3 ppt for methyl bromide and 50 ppt for methyl chloride.
 - (c) The best estimate for the global lifetime of methyl bromide remains at 0.7 (0.5-0.9) years. Additional studies directly related to estimating loss processes for methyl bromide have narrowed the uncertainties slightly, but they do not suggest large revisions to this lifetime. The fraction of emissions derived from industrially produced methyl bromide is unchanged at 10-40% based upon our current understanding of source and sink magnitudes.
- Approaches to further accelerating the date of the recovery of the ozone layer are limited. This Assessment has made hypothetical estimates of the upper limits of improvements that could be achieved if global anthropogenic *production* of ozone-depleting substances were to stop in 2003 or if global anthropogenic *emissions* of ozone-depleting substances were to stop in 2003. Specifically:

Production. Relative to the current control measures (Beijing, 1999) and trends in recent production data, the equivalent effective chlorine atmospheric loading above the 1980 level, integrated from 2002 until the 1980 level is reattained (about 2050), could be decreased by the following amounts:

- 5%, if production of hydrochlorofluorocarbons (HCFCs) were to cease in 2003.
- 4%, if production of chlorofluorocarbons (CFCs) were to cease in 2003.
- 4%, if production of methyl bromide were to cease in 2003.
- 1%, if production of halons were to cease in 2003.
- 0.3%, if production of methyl chloroform were to cease in 2003.

Emissions. Similarly, the equivalent effective chlorine atmospheric loading above the 1980 level, integrated from 2002 until the 1980 level is reattained (about 2050), could be decreased by the following amounts:

- 11%, if emissions of halons were to cease in 2003.
- 9%, if emissions of chlorofluorocarbons (CFCs) were to cease in 2003.
- 9%, if emissions of hydrochlorofluorocarbons (HCFCs) were to cease in 2003.
- 4%, if emissions of methyl bromide were to cease in 2003.
- 3%, if emissions of carbon tetrachloride were to cease in 2003.
- 2%, if emissions of methyl chloroform were to cease in 2003.

The decreases calculated for reduced production and emissions scenarios would be about a factor of 2 smaller if the decreases were compared with the loading integrated from 1980, which is when significant ozone depletion was first detected. Furthermore, the decreases calculated for the integrated equivalent effective chlorine atmospheric loading would be smaller if the cessation in production or emission occurred later than 2003.

The hypothetical elimination of all anthropogenic production of *all* ozone-depleting substances would advance the return of stratospheric loading to the pre-1980 values by about 4 years. The hypothetical elimination of all emissions derived from anthropogenic production of *all* ozone-depleting substances would advance the return of stratospheric loading to the pre-1980 values by about 10 years.

1.1 INTRODUCTION

This chapter provides an update on scientific progress since the previous *Scientific Assessment of Ozone Depletion* (WMO, 1999) regarding ozone-depleting substances (ODSs) in the atmosphere. This includes a discussion of the latest available data for observed trends in the troposphere and stratosphere, emissions, lifetimes, Ozone Depletion Potentials (ODPs), and Global Warming Potentials (GWPs). On the basis of this updated information, we relate observations of ODSs in the atmosphere to expectations, and discuss the evidence that the Montreal Protocol is effectively reducing ozone-depleting gases in the atmosphere.

Also explored in this chapter are the potential future mixing ratios of halocarbons based upon the current Montreal Protocol and recent trends in halocarbon production data. Scenarios are presented to investigate a range of possible future halocarbon mixing ratios. A number of hypothetical “cases” are also explored to demonstrate how production and emission of different ODSs will affect atmospheric halogen burdens in the future.

A discussion of non-ozone-depleting gases, such as carbon dioxide and methane, is also included here. Although they do not participate directly in ozone-destroying reactions, these gases influence stratospheric ozone indirectly by affecting the availability of inorganic chlorine and bromine, or by affecting stratospheric temperatures and thus the occurrence and persistence of polar stratospheric clouds, among other effects.

The discussions here focus on all significant ODSs with atmospheric lifetimes long enough that they are reasonably well mixed in the troposphere. This lifetime cutoff was taken to be 0.5 years. Classic methods for calculating ODPs for gases with lifetimes longer than 0.5 years are assumed to be valid. The details regarding budgets, sources, sinks, ODPs, etc., for gases with shorter lifetimes are discussed in Chapter 2.

1.2 HALOGENATED OZONE-DEPLETING GASES IN THE ATMOSPHERE

Atmospheric measurements of ozone-depleting substances provide a foundation for understanding changes in Earth’s protective ozone layer. Since the previous Assessment (WMO, 1999) additional measurements have refined our understanding of the amounts, distributions, and changes in ozone-depleting gases in the atmosphere. For example, measurements suggest that inorganic chlorine in the stratosphere has now stabilized. This plateau arises as a result of the slow but continued overall

decline in organic chlorine observed globally in the troposphere since 1992-1994. Also, new results from the analysis of firn air provide further evidence that most ozone-depleting gases are entirely of human origin. Details regarding these results and others are found here.

In this chapter and in subsequent ones, the terms concentration, mixing ratio, volume mixing ratio (assuming ideal gas behavior), abundance, amount, and loading refer to dry air mole fraction. These mole fractions are expressed, for example, as parts per trillion (ppt; pmol mol^{-1}). The term “ton” is used to represent a metric ton, which is 10^6 grams. Also, the term “Montreal Protocol” is used to indicate the fully amended and adjusted Montreal Protocol as of 2002 (Beijing Amendments), unless otherwise specified.

1.2.1 Updated Atmospheric Observations of Ozone-Depleting Gases

1.2.1.1 CHLOROFLUOROCARBONS (CFCs)

Updated ground-based measurements of chlorofluorocarbons (CFCs) show continued increases for global surface mixing ratios of CFC-12 (CCl_2F_2). Surface mixing ratios of CFC-113 ($\text{CCl}_2\text{FCClF}_2$) peaked around 1996 and have been decreasing slowly thereafter. The decrease noted for CFC-11 (CCl_3F) mixing ratios in 1996 has continued (Figure 1-1; Table 1-1; Montzka et al., 1999; Prinn et al., 2000). Observed rates of change in the lower atmosphere for all three of these CFCs were slightly smaller in 2000 than in 1996 (Table 1-1; Prinn and Zander et al., 1999). Although emissions of CFC-12 declined substantially during the 1990s, mixing ratios of CFC-12 continue to increase because emissions are still larger than the small losses associated with its long atmospheric lifetime (100 years).

Calibration differences between three global ground-based measurement networks—the Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment/Advanced GAGE (ALE/GAGE/AGAGE; denoted “AGAGE” in this chapter) network, the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL; denoted “CMDL” in this chapter) network, and the University of California at Irvine (UCI) network—are on the order of 1-2% for CFC-11 and -12, and are slightly smaller for CFC-113. The trends measured at Earth’s surface by these three networks are similar in recent years (Table 1-1).

Updated column abundance measurements of CFC-12 from the ground also show continued increases in the atmospheric burden of this gas (Figure 1-2; Zander et al., 2000). The mean rate of accumulation, however, has slowed

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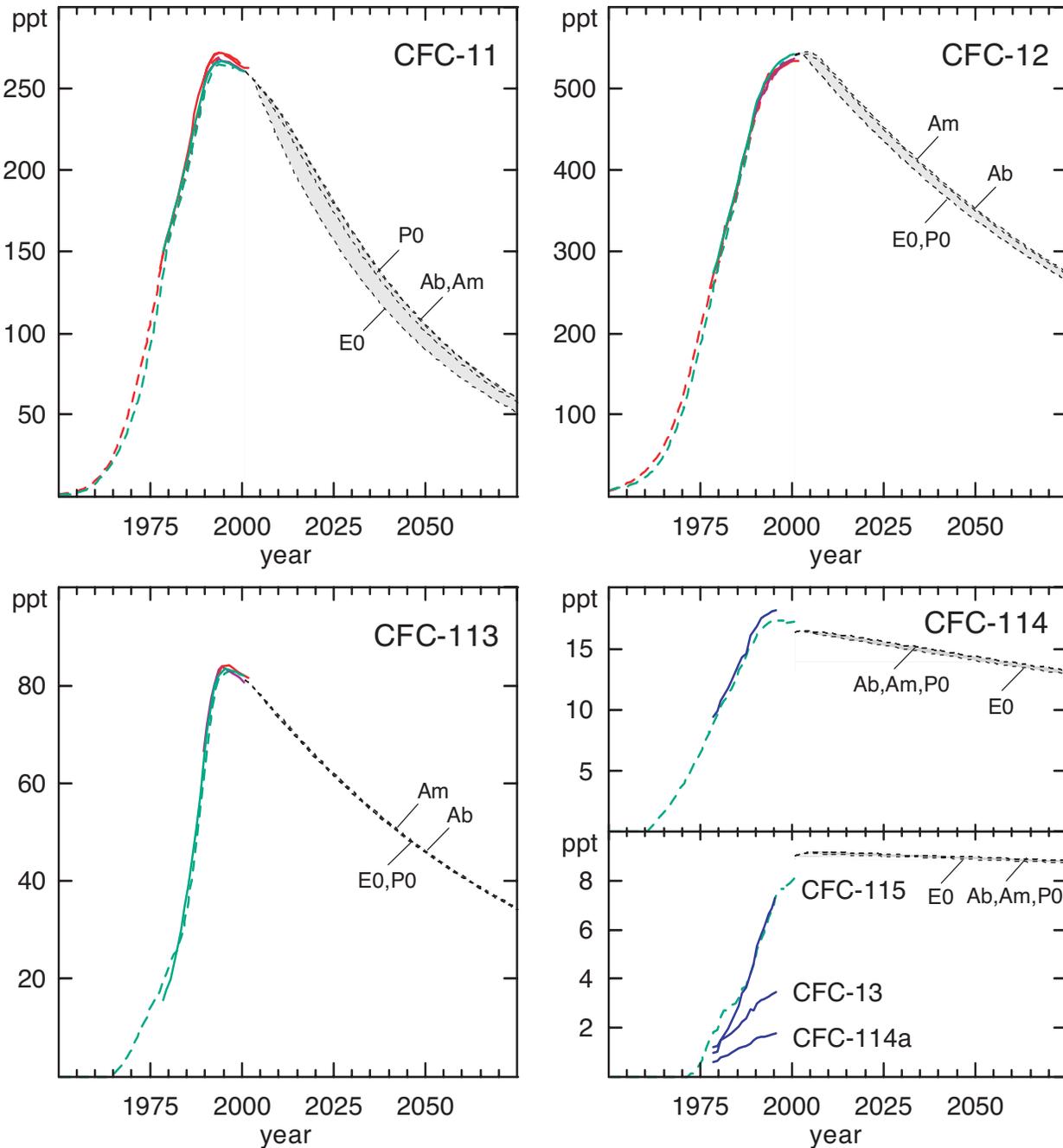


Figure 1-1. Past and potential future atmospheric mixing ratios of CFCs. Measurements of ambient air (solid lines) and histories inferred from measurements of firn air (long-dashed lines) define past burdens at Earth’s surface. Potential future mixing ratios (short-dashed lines) have been calculated for different scenarios that are described in Section 1.8 (Ab, best guess; E0, zero emissions (not attainable, but defines a lower limit); Am, maximum allowed production; P0, zero production). Data sources for measurements of ambient air: AGAGE global monthly means (solid green lines: Prinn et al., 2000); CMDL global monthly means (solid red lines: Montzka et al., 1999); UCI global quarterly means (solid purple lines: D.R. Blake et al., 1996); and University of East Anglia (UEA) results from Cape Grim, Tasmania (for 41°S only) (solid blue lines: Oram, 1999). See the notes to Table 1-1 for more details regarding sampling frequencies and techniques. Antarctic histories have been derived from firn air extracted at the South Pole (red dashed lines: Butler et al., 1999) and Law Dome, Antarctica (green dashed lines: Sturrock et al., 2002). The shading shows the range of mixing ratios encompassed by the future scenarios.

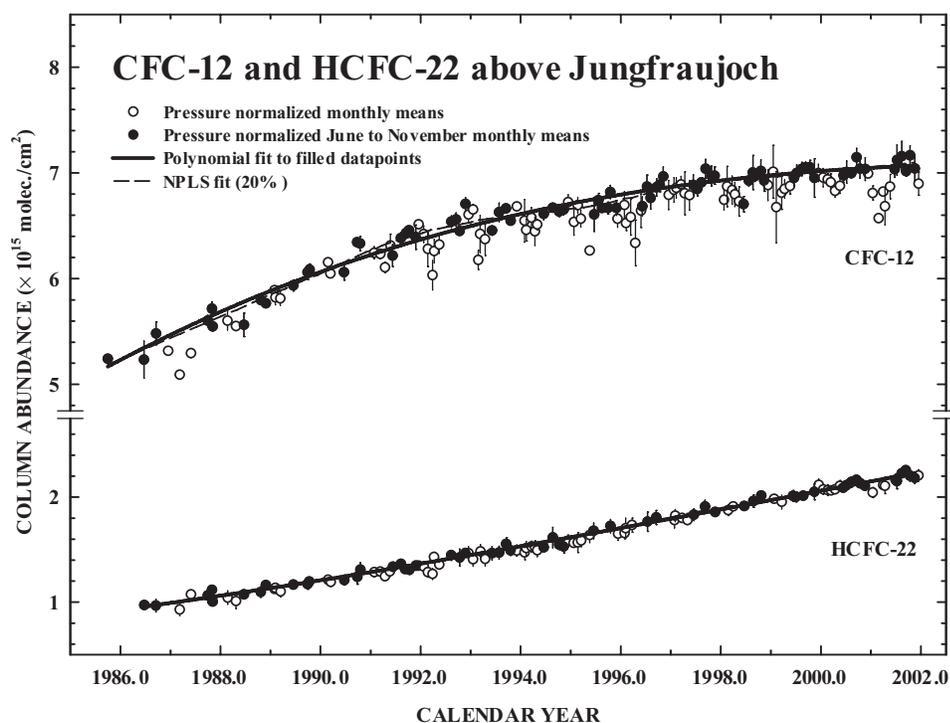


Figure 1-2. The time evolution of the monthly mean vertical column abundances of CFC-12 and HCFC-22 above the Jungfraujoch station, Switzerland, from 1985 to 2002 (update of Zander et al., 2000). Polynomial fits to the June to November columns are represented by the solid lines; nonparametric least-square fits (NPLS, dashed lines) are also shown but are noticeable only for CFC-12.

from 4.97×10^{13} molec $\text{cm}^{-2} \text{yr}^{-1}$ (or $+0.71\% \text{yr}^{-1}$) in 1998 to 3.06×10^{13} molec $\text{cm}^{-2} \text{yr}^{-1}$ (or $+0.43\% \text{yr}^{-1}$) in 2000.

Updated balloon-based measurements at northern midlatitudes also reveal continued increases for CFC-12 in the stratosphere, up to 21 km altitude. Growth rates between 1997 and 2001, however, are between 2 and 3 ppt yr^{-1} , which is less (significant at the 2σ level) than observed between 1978 and 1990, and also less (significant at the 1σ level) than observed between 1990 and 1997 (updated work from Engel et al., 1998).

Measured trends and atmospheric distributions continue to suggest that CFC emissions in 2000 were substantially smaller than in the late 1980s and early 1990s (Montzka et al., 1999; Prinn et al., 2000). The most recent trends and interhemispheric gradients suggest, however, that emissions are not yet insignificant. Persistent mixing ratio gradients (or lack thereof) across latitudes on hemispheric scales can provide some indication of emission locations, but they are generally not useful for delineating emission rates from any individual country despite assertions to the contrary in some studies (Libo et al., 2001).

A number of less abundant CFCs have been measured in the atmosphere. CFC-13 (CClF_3), CFC-114 ($\text{CClF}_2\text{CClF}_2$), and CFC-115 (CClF_2CF_3) have found use as specialist refrigerants (R-13, R-114, R-115), aerosol propellants (CFC-114, -115), and foam-blowing agents (CFC-114). Small amounts of CFC-13 are also emitted during aluminum production (Harnisch, 1997) and during the manufacture of CFC-12. CFC-114a (CCl_2FCF_3),

which is an isomer of CFC-114 ($\text{CClF}_2\text{CClF}_2$), has also been detected in the background atmosphere (Oram, 1999; Culbertson et al., 2000). The most likely origin of CFC-114a is as a byproduct of the CFC-114 production process (Chen et al., 1994).

Measurements of air samples collected at Cape Grim, Tasmania (41°S), show that the abundance of all four of these minor CFCs increased substantially between 1978 and the mid-1990s (Figure 1-1; Table 1-1; Oram, 1999). During the early 1990s, however, the growth rates began to decline and by 1995 had all fallen to below 0.4 ppt yr^{-1} . In late 1995, mixing ratios at Cape Grim were 3.5 ppt (CFC-13), 16.5 ppt (CFC-114), 1.8 ppt (CFC-114a), and 7.5 ppt (CFC-115) (Table 1-1).

More recent measurements from Cape Grim show mid-2000 mixing ratios of about 8 ppt and 16.7 ppt for CFC-115 and -114, respectively (Sturrock et al., 2001). CFC-115 was increasing at 0.1 ppt yr^{-1} , while CFC-114 had stopped growing altogether. Mangani et al. (2000) similarly reported negligible growth for CFC-114 in recent years from samples collected in Antarctica. For these gases, direct comparisons between reported results are difficult because they often do not overlap in time, and, in the case of CFC-114, the AGAGE and Mangani et al. (2000) measurements may include significant contributions from both $\text{C}_2\text{Cl}_2\text{F}_4$ isomers (CFC-114 and -114a).

Culbertson et al. (2000) measured CFC-13 and -114a in air samples collected at a rural, continental site in the United States in March-April 2000. The mean

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Table 1-1. Mixing ratios and growth rates of some important ozone-depleting substances.

Chemical Formula	Common or Industrial Name	Mixing Ratio (ppt)			Growth (1999-2000)		Laboratory, Method
		1996	1998	2000	(ppt yr ⁻¹)	(% yr ⁻¹)	
CFCs							
CCl ₂ F ₂	CFC-12	532.4	538.4	542.9	2.3	0.42	AGAGE, in situ ^a
		525.9	531.0	534.5	1.9	0.35	CMDL, in situ ^a
		523.2	529.3	534.0	1.8	0.34	CMDL, flasks ^a
		526.2	532.0	535.7	1.9	0.35	UCI, flasks ^a
CCl ₃ F	CFC-11	265.6	263.0	260.5	-1.1	-0.41	AGAGE, in situ ^a
		270.5	267.2	263.2	-2.0	-0.76	CMDL, in situ ^a
		269.5	265.9	262.6	-1.5	-0.56	CMDL, flasks ^a
		266.3	263.7	261.0	-1.0	-0.39	UCI, flasks ^a
CClF ₃	CFC-13	3.5					UEA, SH, flasks ^b
CCl ₂ FCClF ₂	CFC-113	83.2	82.9	82.0	-0.35	-0.43	AGAGE, in situ ^a
		84.2	83.0	82.1	-0.32	-0.39	CMDL, flasks ^b
		83.1	82.1	81.1	-0.49	-0.60	UCI, flasks ^a
CClF ₂ CClF ₂	CFC-114	16.5					UEA, SH, flasks ^b
CCl ₂ FCF ₃	CFC-114a	1.8					UEA, SH, flasks ^b
	CFC-114, -114a		17.1	17.2	-0.10	-0.58	AGAGE, in situ ^b
CClF ₂ CF ₃	CFC-115		7.8	8.1	0.16	0.20	AGAGE, in situ ^b
		7.5					UEA, SH, flasks ^b
Halons							
CBrClF ₂	Halon-1211		3.9	4.1	0.13	3.2	AGAGE, in situ ^b
		3.5	3.8	4.0	0.10	2.5	CMDL, flasks ^{a, b}
		3.4	3.6	3.9	0.12	3.2	UCI, flasks ^a
		3.8	4.2	4.4	0.13	2.9	UEA, SH, flasks ^b
CBrF ₃	Halon-1301		2.8	2.9	0.08	2.8	AGAGE, in situ ^b
		2.3	2.5	2.6	0.06	2.4	CMDL, flasks ^a
		2.0	2.2	2.3	0.05	2.2	UEA, SH, flasks ^b
CBrF ₂ CBrF ₂	Halon-2402	0.48					CMDL, flasks ^b
		0.42	0.42	0.43	0.001	0.2	UEA, SH, flasks ^b
CBr ₂ F ₂	Halon-1202	0.037	0.044				UEA, SH, flasks ^b
Chlorocarbons —see also Chapter 2							
CH ₃ Cl	Methyl chloride		538	536			AGAGE, SH, in situ ^b
		588					OGI, flasks ^c
CCl ₄	Carbon tetrachloride	100.5	98.2	96.1	-0.94	-0.97	AGAGE, in situ ^a
		103.2	101.9	99.6	-0.95	-0.95	CMDL, in situ ^a
		103.1	101.4	99.2	-1.03	-1.03	UCI, flasks ^a
CH ₃ CCl ₃	Methyl chloroform	90.3	64.6	45.4	-8.7	-17	AGAGE, in situ ^a
		96.9	68.9	46.4	-10.2	-20	CMDL, in situ ^a
		92.3	65.7	45.7	-9.1	-18	CMDL, flasks ^b
		93.6	71.7	47.6	-13.0	-24	UCI, flasks ^a
HCFCs							
CHClF ₂	HCFC-22	122.4	132.7	143.2	5.4	3.8	AGAGE, in situ ^a
		121.5	131.4	141.9	5.1	3.7	CMDL, flasks ^b
CH ₃ CCl ₂ F	HCFC-141b		9.5	13.0	1.8	15	AGAGE, in situ ^b
		5.4	9.1	12.7	1.7	15	CMDL, flasks ^b
		4.3					UT, flasks ^b

Table 1-1, continued.

Chemical Formula	Common or Industrial Name	Concentration (ppt)			Growth (1999-2000)		Laboratory, Method
		1996	1998	2000	(ppt yr ⁻¹)	(% yr ⁻¹)	
CH ₃ CClF ₂	HCFC-142b		10.4	12.5	1.1	9.4	AGAGE, in situ ^b
		7.7	9.6	11.7	1.0	8.9	CMDL, flasks ^b
		9.2					UT, flasks ^b
CHCl ₂ F	HCFC-21	0.29					UEA, SH, flasks ^b
CHCl ₂ CF ₃	HCFC-123	0.03					UEA, SH, flasks ^b
CHClFCF ₃	HCFC-124		0.89	1.34	0.35	30	AGAGE, in situ ^b
Bromocarbons —see also Chapter 2							
CH ₃ Br	Methyl bromide		9-10				Many ^d
			8.4	8.1			AGAGE, SH, in situ ^b

Global mixing ratios and growth rates at Earth's surface unless otherwise specified. AGAGE: 4-5 in situ electron capture detection (ECD) sampling sites, 2 in situ gas chromatography-mass spectrometry (GC-MS) sampling sites, 2 flask sampling sites; CMDL: 5 in situ sampling sites, 8-10 remote flask sampling sites; UEA: University of East Anglia, analysis of archive flasks and regularly sampled flasks filled at Cape Grim, Australia (41°S); UCI: quarterly sampling from a multitude of sites between 47°S and 71°N.; UT: University of Tokyo, 2 flask sampling sites; OGI: Oregon Graduate Institute, quarterly flask sampling at ~40 sites. NH, Northern Hemisphere; SH, Southern Hemisphere.

Data sources: AGAGE: Prinn et al. (2000); Sturrock et al. (2001); ftp://cdiac.esd.ornl.gov/pub/ale_gage_Agag. CMDL: Butler et al. (1999); Montzka et al. (1999, 2000); Hall et al. (2002); <http://www.cmdl.noaa.gov>. UEA: Fraser et al. (1999); Oram et al. (1995); Oram (1999). UCI: D.R. Blake et al. (1996); N.J. Blake et al. (2001). UT: Shirai and Makide (1998).

^a Measurements by gas chromatography with electron capture detection.

^b Measurements by gas chromatography with mass spectrometry detection.

^c Results from OGI for CH₃Cl have been scaled by 550/600; see Kurylo and Rodriguez et al. (1999).

^d See Section 1.5.

mixing ratio of CFC-13 was 3.6 ± 0.3 ppt, which is in reasonable agreement with the measurements of Oram (1999). Conversely, the mixing ratio of CFC-114a was 7.9 ± 0.8 ppt, which is substantially higher than that reported by Oram (1999).

1.2.1.2 HALONS

Although the phaseout was imposed on halon production in developed countries earlier than for all other halocarbons, mixing ratios of both Halon-1211 (CBrClF₂) and Halon-1301 (CBrF₃) continued to increase in the atmosphere in 2000 (Figure 1-3). Global surface mixing ratios of individual halons were less than 5 ppt in 2000 (Table 1-1). Since the previous Assessment (WMO, 1999) a new set of regular measurements has become available (Prinn et al., 2000; Sturrock et al., 2001). Among the laboratories studying long-term trends of halons in the atmosphere, calibration differences are about 10-15% (UCI < CMDL < AGAGE < University of East Anglia (UEA)) for Halon-1211 and about 25% (UEA < CMDL < AGAGE) for Halon-1301 (Butler et al., 1998; Fraser et al., 1999; Montzka et al., 1999).

For Halon-1211, all four laboratories report rates of increase in 2000 of about 3% yr⁻¹, or 0.1 to 0.13 ppt yr⁻¹ (Table 1-1). For Halon-1301, CMDL, UEA, and

AGAGE data suggest rates of increase of 0.05-0.08 ppt yr⁻¹ or 2-3% yr⁻¹ in 2000 (Table 1-1). For both these halons, these rates of increase are only slightly slower than observed during the first half of the 1990s.

Two less abundant halons have been further monitored in the atmosphere. Halon-2402 (CBrF₂CBrF₂) is present at between 0.4 and 0.5 ppt in the global atmosphere (Table 1-1; Butler et al., 1998; Fraser et al., 1999), and its rate of increase has slowed dramatically since the mid-1990s (Fraser et al., 1999; Figure 1-3). Halon-1202 (CBr₂F₂) has been measured in background air at mixing ratios of 0.04-0.05 ppt (Table 1-1; Figure 1-3; Engen et al., 1999; Fraser et al., 1999). During 1995-1996 the abundance of Halon-1202 was increasing at 17% yr⁻¹ (0.007 ppt yr⁻¹) in the Southern Hemisphere, although updated measurements by UEA suggest that this rate is much smaller now (Figure 1-3). Although this halon has been used by the military in a few minor applications, most is produced from over-bromination during the production of Halon-1211 (UNEP, 1998b).

1.2.1.3 CARBON TETRACHLORIDE (CCl₄)

Global surface mixing ratios of carbon tetrachloride (CCl₄) have decreased since about 1990; mixing ratios in 2000 were between 95 and 100 ppt (Figure 1-4; Table

SOURCE GASES

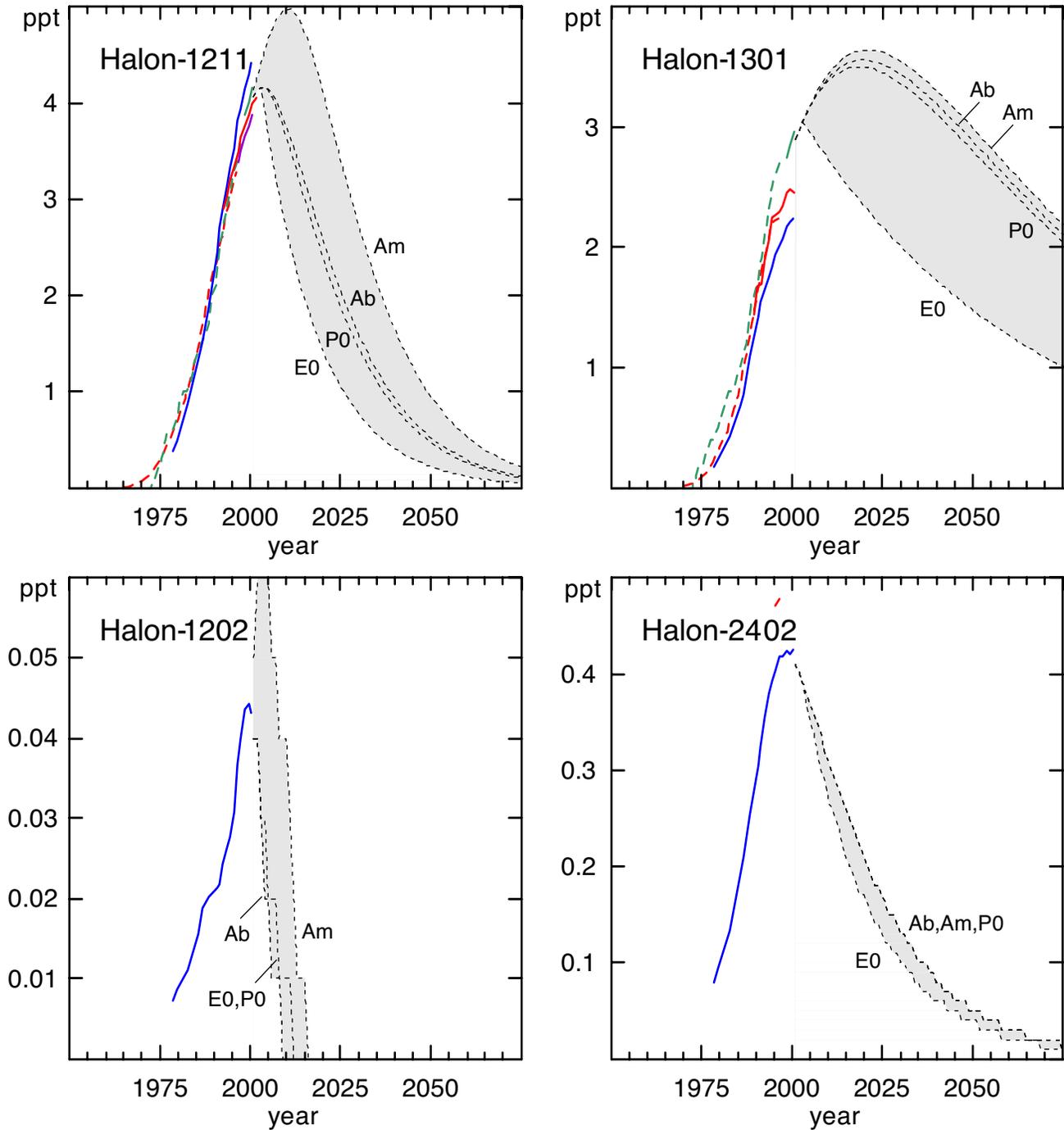


Figure 1-3. Past and potential future atmospheric mixing ratios of halons. Measurements of ambient air (solid lines) and histories inferred from measurements of firn air (long-dashed lines) define past burdens at Earth’s surface. Potential future mixing ratios (short-dashed lines) have been calculated for different scenarios that are described in Section 1.8 and the caption to Figure 1-1. Data inferred from firn air are from the same sources as described in Figure 1-1. Data sources for measurements of ambient air: UEA from Cape Grim, Tasmania (for 41°S only) (solid blue lines: Fraser et al., 1999); AGAGE global mean data (solid green lines: Sturrock et al., 2001); UCI global quarterly means (solid purple lines: Blake et al., 2001); and CMDL global means (solid red lines: Butler et al., 1998; Montzka et al., 1999). The shading shows the range of mixing ratios encompassed by the future scenarios. See the notes to Table 1-1 for more details regarding sampling frequencies and techniques.

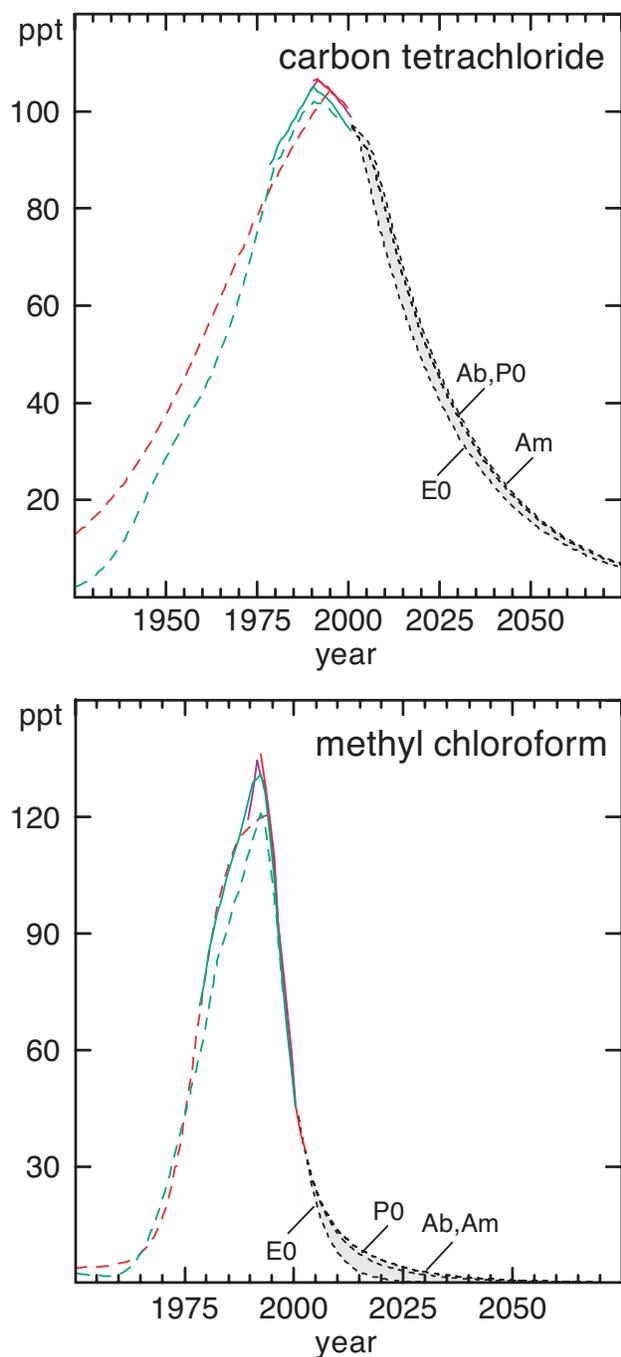


Figure 1-4. Past and potential future atmospheric mixing ratios of carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3). Measurements of ambient air (solid lines) and histories inferred from measurements of firn air (long-dashed lines) define past burdens at Earth's surface. Potential future mixing ratios (short-dashed lines) have been calculated for different scenarios that are described in Section 1.8 and the caption to Figure 1-1. Data sources and shading are the same as described in Figure 1-1.

1-1; Simmonds et al., 1998a; Montzka et al., 1999; Prinn et al., 2000). The observed rates of change have remained fairly constant since 1993 at about $-1\% \text{ yr}^{-1}$ or -1 ppt yr^{-1} . The interhemispheric difference has also been fairly constant at about 2% (North > South) since 1993 and suggests that significant emissions of carbon tetrachloride remain (see Section 1.6). Calibration differences between CMDL, UCI, and AGAGE are 3 to 4%.

1.2.1.4 METHYL CHLOROFORM (CH_3CCl_3)

The rapid decline in emissions of methyl chloroform (CH_3CCl_3) and its relatively short lifetime have together resulted in rapidly decreasing mixing ratios in recent years (Figure 1-4; Montzka et al., 2000; Prinn et al., 2001). The global mean surface mixing ratio in 2000 was approximately 46 ppt (Table 1-1), compared with the maximum of 130 ppt observed in 1992. Hemispheric differences were 2 to 3% in 2000, or much smaller than in earlier years.

Fairly constant exponential decay with a time constant of $(5.5 \text{ yr})^{-1}$ was observed for methyl chloroform during 1998-2000 (Montzka et al., 2000). This implies that the absolute rate of decline for methyl chloroform is becoming smaller: it peaked at -14 to -15 ppt yr^{-1} in 1995-1996, and was one-third less in 1999-2000, or about -10 ppt yr^{-1} (Table 1-1).

Scale differences between CMDL and AGAGE were stated as being $\sim 10\%$ in Prinn and Zander et al. (1999), and even larger among a broader range of laboratories. Since then scale revisions by AGAGE (Scripps Institution of Oceanography (SIO), SIO-93 to SIO-98; Prinn et al., 2000) and CMDL (Hall et al., 2002) suggest that the AGAGE-CMDL differences are now on the order of $<3\%$. There is a small time dependence to this difference. Similar mixing ratios are reported by UCI in 2000 (Table 1-1).

1.2.1.5 HYDROCHLOROFLUOROCARBONS (HCFCs)

Updated measurements of hydrochlorofluorocarbons (HCFCs) indicate that global mixing ratios of the three most abundant HCFCs continue to increase in the atmosphere, owing to sustained emissions (Figure 1-5). Updated measurements suggest global mixing ratios for HCFC-22 (CHClF_2) of 140-145 ppt in 2000 and a fairly constant growth rate of about 5 ppt yr^{-1} (Table 1-1; Figure 1-5; Simmonds et al., 1998b; Montzka et al., 1999). Sturrock et al. (2001) reported slightly faster increases from samples collected only at Cape Grim, Tasmania (6.3 ppt yr^{-1}). Hemispheric differences have been fairly constant in recent years at about 10% (North > South).

SOURCE GASES

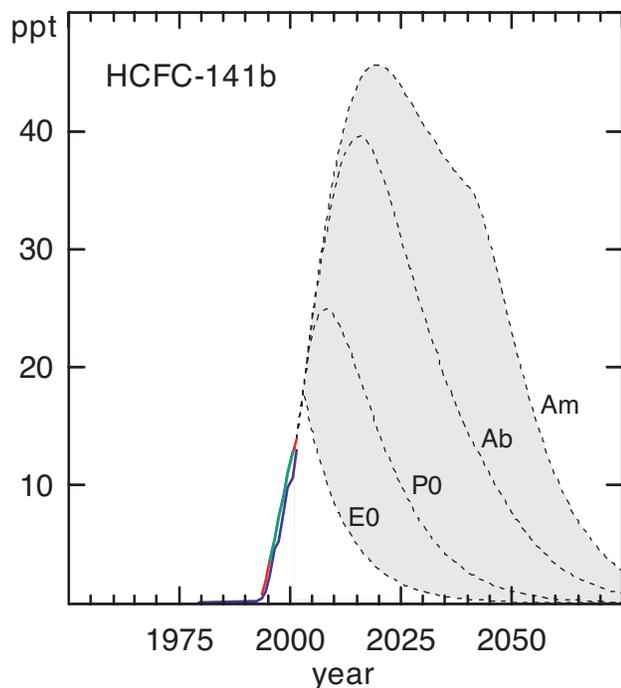
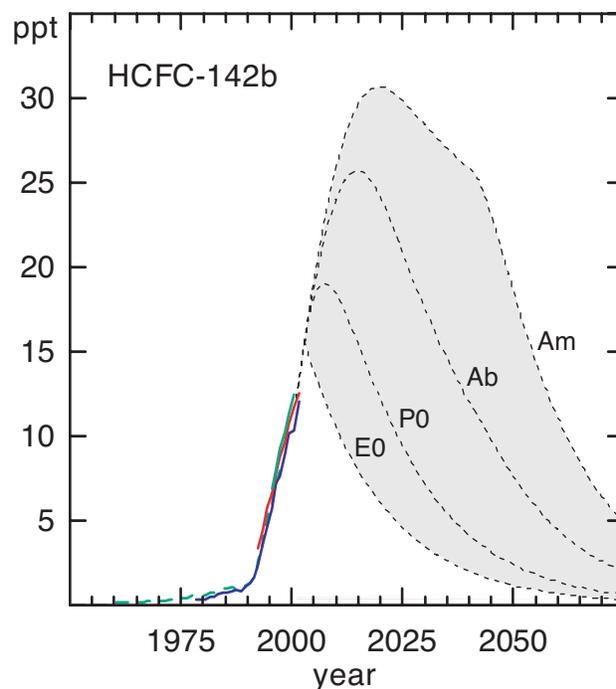
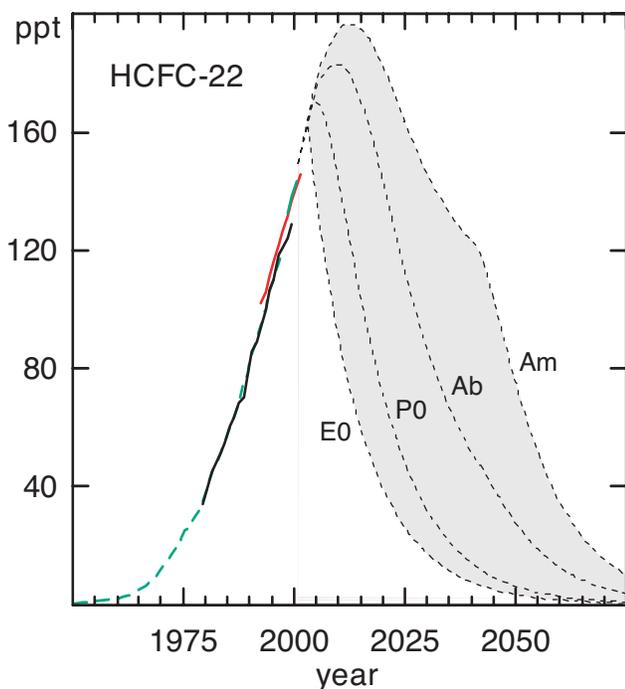


Figure 1-5. Past and potential future atmospheric mixing ratios of HCFCs. Measurements of ambient air (solid lines) and histories inferred from measurements of firn air (long-dashed lines) define past burdens at Earth's surface. Potential future mixing ratios (short-dashed lines) have been calculated for different scenarios that are described in Section 1.8 and the caption to Figure 1-1. Data sources: mixing ratios from Antarctic firn (long-dashed green line: Sturrock et al., 2002); AGAGE global means (solid green lines: Prinn et al., 2000; Sturrock et al., 2001); CMDL global means (solid red lines: Montzka et al., 1999); UEA from Cape Grim, Tasmania (for 41°S only) (solid blue lines: Oram et al., 1995); SIO from Cape Grim (41°S only) (solid black line: Miller et al., 1998). See the notes to Table 1-1 for more details regarding sampling frequencies and techniques. The shading shows the range of mixing ratios encompassed by the future scenarios.

Mean total column abundances of HCFC-22 measured above the Jungfraujoch station, Switzerland, in 1995 were 1.66×10^{15} molec cm^{-2} , increasing by 8.71×10^{13} molec $\text{cm}^{-2} \text{yr}^{-1}$ (or $5.2\% \text{yr}^{-1}$); for 2000, these figures were 2.11×10^{15} molec cm^{-2} , increasing by 8.93×10^{13} molec $\text{cm}^{-2} \text{yr}^{-1}$ (or $4.2\% \text{yr}^{-1}$), thus indicating that the absolute rate of atmospheric accumulation during those 5 years did not change substantially (Figure 1-2; an update of Zander et al., 2000).

Updated measurements show that the global mean surface mixing ratio of HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$) rose from about 5 ppt in mid-1996 to nearly 13 ppt in mid-2000 (Table 1-1; Figure 1-5; Montzka et al., 1994, 1999; Simmonds et al., 1998b; Prinn et al., 2000; Sturrock et al., 2001). The current growth rate is slightly less than 2ppt yr^{-1} . Northern Hemispheric mean mixing ratios were approximately 3 ppt higher than Southern Hemispheric means in mid-2000.

Global mean surface mixing ratios of HCFC-142b (CH_3CClF_2) have risen from 7 to 8 ppt in mid-1996 to about 12 ppt in mid-2000, with a current growth rate of 1.0 ppt yr^{-1} (Table 1-1; Figure 1-5; Montzka et al., 1994; 1999; Simmonds et al., 1998b; Prinn et al., 2000; Sturrock et al., 2001). Northern Hemispheric means were 2 to 2.5 ppt higher than Southern Hemispheric means in mid-2000. Calibration differences are about 5% or less for HCFC-22, -141b, and -142b among laboratories reporting results recently (Table 1-1).

Since the previous Assessment, three other HCFCs have been reported in the background atmosphere: HCFC-123 (CHCl_2CF_3), HCFC-124 ($\text{CHClF}_2\text{CF}_3$), and HCFC-21 (CHCl_2F) (Table 1-1). From measurements at Cape Grim, Sturrock et al. (2001) reported late-1998 tropospheric mixing ratios of 0.53 ppt and 0.1 ppt for HCFC-124 and -123, respectively, the former having a growth rate of 0.06 ppt yr^{-1} (13%). Oram (1999) found similarly low levels of HCFC-123 at Cape Grim from archived samples collected between 1978 and 1993, but noted that the mixing ratio doubled between 1990 and 1993. Oram (1999) also reported measurements of HCFC-21 over the same period. Mixing ratios were typically in the range 0.2-0.4 ppt, with no significant trend.

1.2.1.6 METHYL BROMIDE (CH_3Br)

Our understanding of the concentration of methyl bromide (CH_3Br) in the atmosphere during the 1990s remains much the same as was given in the previous (1998) Assessment (WMO, 1999). No new global trends have been reported since those of Khalil et al. (1993). Recent data from research cruises encompassing a wide latitudinal span in both hemispheres (Yokouchi et al., 2000a; Li et al., 2001; Groszko and Moore, 1998; King et al., 2000), from aircraft missions (Schauffler et al., 1999), and from two midlatitude, ground-based sites (Miller, 1998) suggest that the mean global mixing ratio of atmospheric CH_3Br ranged from 9 to 10 ppt before reductions in industrial production began in the late 1990s, consistent with that reported in the 1998 Assessment. These new studies, along with that of Wingenter et al. (1998), suggest that the best estimate of the global, area-weighted, mean hemispheric ratio lies between 1.2 and 1.3 (North > South). This hemispheric ratio varies seasonally from 1.1 to 1.4, driven mainly by seasonality in Northern Hemispheric mixing ratios. Recent published comparisons between the National Center for Atmospheric Research (NCAR) and UCI show measurements agreeing within an average of 7% (Schauffler et al., 1999).

The vertical distributions and weak tropospheric gradient observed by N.J. Blake et al. (1996; 1997) are supported by measurements of Schauffler et al. (1999).

The tropospheric gradient in mixing ratio of 3-14% reported by Schauffler et al. (1999) is consistent with that reported in the 1998 Assessment, which noted a 0-15% vertical gradient in the tropospheric mixing ratio. Additionally Schauffler et al. (1999) noted that CH_3Br mixing ratios in the lower stratosphere (20 km) were reduced by 40% in the tropics and by 70% at Northern Hemispheric midlatitudes (July) relative to amounts observed in the troposphere.

1.2.1.7 METHYL CHLORIDE (CH_3Cl)

Khalil and Rasmussen (1999) recently published a detailed analysis of global measurements of methyl chloride (CH_3Cl) conducted over 16 years (1981-1997) at locations distributed throughout both hemispheres, during which methyl chloride reportedly decreased by about 4%. As noted in Chapter 2 of the 1998 Assessment (Kurylo and Rodríguez et al., 1999), Khalil and Rasmussen's global mean mixing ratio of 606 ppt is somewhat higher than the average of 550 ± 30 ppt obtained by other investigators. New results continue to suggest global means closer to 550 ppt than 600 ppt (Sturrock et al., 2001; Yokouchi et al., 2000b; Table 1-1). Khalil and Rasmussen (1999) reported a mean annual latitudinal distribution in the CH_3Cl mixing ratio in which the tropics were about 40 ppt higher than the poles, and they inferred that this had to be caused by a tropical terrestrial source. They also reported a seasonal cycle with an amplitude of about 10%, explicable mainly in terms of seasonal changes in hydroxyl radical (OH) abundance. In more recent work involving land-based and shipboard measurements extending from the Canadian Arctic through the Pacific and Indian Oceans to the Antarctic between 1996 and 1998, Yokouchi et al. (2000b) found CH_3Cl mixing ratios ranging from 500 ppt in the high Arctic and Antarctic to 570 ppt near the equator. Although this latitudinal distribution was measured only over a fraction of a year, it is similar to the annual mean distribution reported by Khalil and Rasmussen (1999).

1.2.2 Twentieth Century Atmospheric Histories for Halocarbons from Firn Air

Since the previous Assessment (WMO, 1999), 20th century atmospheric histories for halocarbons have been reconstructed from the analysis of air trapped in snow above glaciers, also known as firn air (Figures 1-1, 1-3, 1-4, and 1-5; Butler et al., 1999; Sturges et al., 2001a; Sturrock et al., 2002). Conclusions drawn from the firn-air results rely on the assumption that these halocarbons are neither produced nor destroyed in the firn. These firn-

SOURCE GASES

air data show that mixing ratios of CFCs, halons, and HCFCs in the oldest air sampled are generally less than 2% of the amounts measured today in the background atmosphere. Furthermore, and consistent with these halocarbons not being destroyed or produced in firm air over time, the 20th century atmospheric histories reconstructed from firm-air results and firm diffusion models are reasonably consistent with calculated histories based on records of industrial halocarbon production (Prinn et al., 2000). Somewhat higher amounts of carbon tetrachloride (5 ppt) and methyl chloroform (2-4 ppt) have been reported in the deepest and oldest samples, although these amounts were close to the detection limit of the instruments used in these analyses. These results suggest that nonindustrial sources of these halocarbons are insignificant.

Mixing ratios for methyl chloride and methyl bromide were only 10-30% lower than present day in firm air from Antarctica dating back to the early 1900s (Butler et al., 1999; Sturges et al., 2001a). The results are consistent with the presence of substantial nonindustrial emissions of these gases. Consistent results were observed for methyl bromide in firm samples at four different locations in Antarctica. These suggest that levels of methyl bromide in the Southern Hemisphere have increased by about 3 ppt since the early 20th century and about 2 ppt since the mid-20th century (see Section 1.5). Unfortunately, Northern Hemispheric firm-air profiles of methyl bromide show significant anomalies near the snow-ice transition, a feature not observed in the Antarctic profiles. For methyl chloride, firm data from both hemispheres suggest that the atmospheric burden over the last half of the 20th century

increased by about 10%. Additional details and discussion of these results appear in Section 1.5.

1.2.3 Total Atmospheric Chlorine

1.2.3.1 TOTAL ORGANIC CHLORINE IN THE TROPOSPHERE

Total organic chlorine (CCl_y) contained in long-lived chlorine-bearing source gases continues to decrease slowly in the lower atmosphere. In mid-2000, CCl_y was ~3.5 parts per billion (ppb) (Table 1-2), or about 5% lower than the peak observed in 1992-1994. The decrease still results primarily from the exponential decline observed for methyl chloroform (Table 1-2; Table 1-1; Figure 1-4). This situation is changing, however, because the absolute rate of decrease observed in 1999-2000 for methyl chloroform had diminished by one-third compared with 1995-1996 and will continue to lessen in the future (Montzka et al., 1999; see also Section 1.8).

By 2000 total chlorine from aggregated CFCs was no longer increasing (Table 1-2). Continued increases in chlorine from CFC-12 (3.6-4.6 ppt Cl yr^{-1}) in 2000 were similar in magnitude to declines in chlorine from the sum of CFC-11 and CFC-113 (Table 1-1).

The rate of increase in chlorine from HCFCs has been fairly constant since 1996 (Tables 1-1 and 1-2). HCFC-22 accounts for approximately 80% of chlorine from HCFCs in today's atmosphere and for about half of the annual increase in chlorine from all HCFCs (5 ppt Cl yr^{-1} out of about 10 ppt Cl yr^{-1}). Continued increases in

Table 1-2. Contributions of halocarbons to total organic chlorine (CCl_y) in the troposphere.

	Total CCl_y (ppt Cl)		Contribution to Total CCl_y (%)		Rate of Change in Total CCl_y (ppt Cl yr^{-1})	
	1996	2000	1996	2000	1996	2000
Aggregate CFCs	2161	2156	59	61	7.1	-0.6
CH_3Cl	550	550	15	16	0.0	0.0 ^a
CCl_4	407	384	11	11	-4.0	-3.8
Aggregate HCFCs	142	182	4	5	10.3	9.7
CH_3CCl_3	278	139	8	4	-40.8	-27.2
Short-lived gases ^b	100	100	3	3	0.0 ^a	0.0 ^a
Halon-1211	4	4	0	0	0.2	0.1
Total CCl_y	3642	3516			-27 (-0.8% yr^{-1})	-22 (-0.6% yr^{-1})

Bold-faced type is used to highlight the largest changes from 1996 to 2000. Some differences for 1996 from WMO (1999) arise because of small recent adjustments to absolute calibration scales and because the results presented here are an average of AGAGE and CMDL global means. Similar conclusions could be drawn with data from UCI (Table 1-1).

^a Presumed to be zero; not well documented.

^b Gases such as CH_2Cl_2 , CHCl_3 , and C_2Cl_4 .

HCFC-141b and -142b mixing ratios account for the additional annual chlorine increase.

The four minor CFCs accounted for about 50 ppt of Cl, or less than 1.5% of the total tropospheric chlorine burden in 2000 (CFC-13, -114, -114a, and -115). About 70% of this 50 ppt is from CFC-114. The current rate of growth for chlorine in these minor CFCs is small (<1 ppt Cl yr⁻¹; Table 1-1).

1.2.3.2 TOTAL INORGANIC CHLORINE IN THE STRATOSPHERE

In a stratosphere unperturbed by polar stratospheric clouds or recent volcanism, more than 95% of inorganic chlorine (Cl_y) is accounted for by the two reservoirs hydrogen chloride (HCl) and chlorine nitrate (ClONO₂) (Zander et al., 1992, 1996). Furthermore, because tropospheric HCl and ClONO₂ mixing ratios are small, the sum of their vertical column abundances is a good surrogate of the Cl_y loading and its evolution in the stratosphere. Past reports of total column abundances of HCl and ClONO₂, as well as their sum (Cl_y) derived from observations at Jungfraujoch (Switzerland, 46.5°N) through 1999, showed increases commensurate with trends in CCl₄ at Earth's surface but delayed by 3-4 years owing to air transport rates between the troposphere and the stratosphere (Prinn and Zander et al., 1999; Mahieu et al., 2000).

An update of measurements from the Jungfraujoch now shows that the monthly mean total column abundances of HCl and ClONO₂ have stopped increasing (Figure 1-6). Updates of column abundance measurements of HCl at Kitt Peak (Arizona, U.S., 31.9°N) (Rinsland et al., 1991; Wallace et al., 1997) and of HCl and ClONO₂ at Lauder (New Zealand, 45°S) (Matthews et al., 1989; Reisinger et al., 1995) also show similar overall long-term trends. These results provide robust evidence that the loading of inorganic Cl_y in the unperturbed stratosphere has recently stabilized in response to the production regulations on ozone-depleting substances outlined in the Montreal Protocol. Within the uncertainty of these measurements, the trends in total column HCl and ClONO₂ are consistent with the trends for chlorinated organic trace gases measured at Earth's surface.

1.2.3.3 HYDROGEN CHLORIDE (HCl) AT 55 KM ALTITUDE IN THE STRATOSPHERE

An independent assessment of total Cl_y near the stratopause has been provided by measurements of HCl made since 1991 at 55 km altitude by the Halogen Occultation Experiment (HALOE) instrument aboard the Upper Atmosphere Research Satellite (UARS) (Russell et al., 1996; Prinn and Zander et al., 1999). At that altitude,

most Cl_y (~93-95%, globally) is in the form of HCl. The broad changes in mean global HCl at 55 km measured by HALOE show a period of monotonically increasing HCl mixing ratios before 1997, and much slower mean changes thereafter (updates to Anderson et al., 2000; Figure 1-7). These long-term trends are consistent with expectations from ground-based measurements after considering lag times associated with transport of tropospheric air to the stratosphere and stratospheric mixing processes (Waugh et al., 2001; Hall and Plumb, 1994).

What remain unexplained in the HALOE HCl data are abrupt changes that occurred over shorter periods, such as those observed in early 1997 (Waugh et al., 2001; Engel et al., 2002) and in 2000 (Figure 1-7). These changes strongly suggest that additional atmospheric processes affect trends in HCl at 55 km (Randel et al., 1999; Considine et al., 1999). Several possible mechanisms likely to cause the early-1997, abrupt peaking of Cl_y at 55 km altitude were considered by Waugh et al. (2001) (such as changes in transport and chemistry partitioning), but none could explain a sharp decrease as early as 1997 in upper stratospheric Cl_y, given the measured tropospheric halocarbon trends and our understanding of atmospheric transport rates and mixing processes. HALOE measurements of methane, however, are anticorrelated with HCl since 1997. This suggests that transport may contribute to the variability observed in the HCl record, but transport effects alone do not resolve these tendencies (personal communication, J. Russell III, Hampton University, U.S., 2001).

1.2.3.4 STRATOSPHERIC CHLORINE COMPARED WITH TROPOSPHERIC CHLORINE

Evaluations of total chlorine (Cl_{tot}) in the stratosphere have been derived from measurements of CCl₄ and Cl_y throughout the stratosphere with the Atmospheric Trace Molecule Spectroscopy (ATMOS) shuttle-based Fourier transform infrared (FTIR) spectrometer (Gunson et al., 1996). Average stratospheric Cl_{tot} was measured at 2.58 ± 0.10 ppb in 1985 (Zander et al., 1992) and 3.53 ± 0.10 ppb in 1994 (Zander et al., 1996). From measurements of a suite of chlorine-bearing source-, sink-, and reservoir species with a balloonborne FTIR spectrometer launched on 8 May and on 8 July 1997 from Fairbanks (Alaska, 64.8°N), Sen et al. (1999) derived a nearly constant value of Cl_{tot}, equal to 3.7 ± 0.2 ppb between 9 and 38 km altitude. Each of these studies confirmed that the bulk of inorganic stratospheric chlorine is well explained by the photodissociation of organic source gases measured in the troposphere after considering time lags associated with air transport and mixing processes.

SOURCE GASES

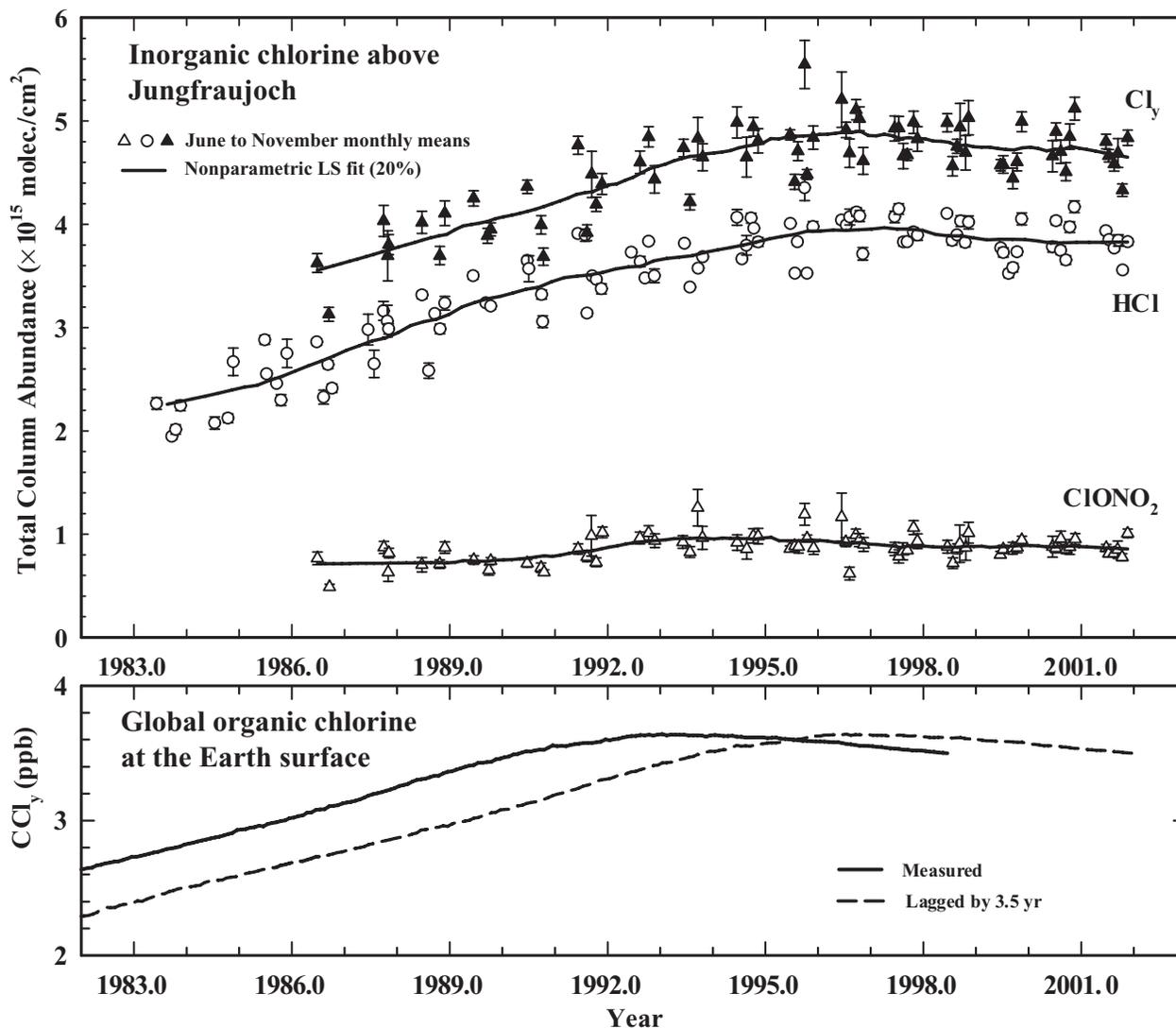


Figure 1-6. Upper frame: Time series of June to November (to avoid significant variability during winter and spring periods) monthly mean vertical column abundances of HCl (open circles) and ClONO₂ (open triangles) derived from solar observations at the Jungfraujoch between 1983 and 2001 (update from Mahieu et al., 2000). Inorganic chlorine (Cl_y, filled triangles) is obtained by summing the HCl and ClONO₂ column measurements. Lines represent nonparametric least-squares fits with 20% weighting. Lower frame: The temporal evolution of global organic chlorine loading (CCl_y) determined from in situ measurements at the ground (solid line: Prinn et al., 2000), and CCl_y lagged by 3.5 years (dashed line).

1.2.4 Total Atmospheric Bromine

1.2.4.1 TOTAL ORGANIC BROMINE IN THE TROPOSPHERE

Total organic bromine (CBr_y) in the troposphere results primarily from surface emissions of methyl bromide, halons, and short-lived bromocarbons. Recent trends in CBr_y are uncertain because global atmospheric trends in methyl bromide since 1992 are not yet well doc-

umented. Firn-air measurements suggest significant increases for this gas during 1900-1998, but they do not tightly constrain recent atmospheric trends. Changes in the growth rate of methyl bromide are perhaps likely during the 1990s because of the restrictions placed on industrial production in developed countries then (see the fully revised and amended Montreal Protocol).

Total organic bromine from halons has continued to increase since 1996 owing to continued anthropogenic production and use. The aggregate contribution of halons

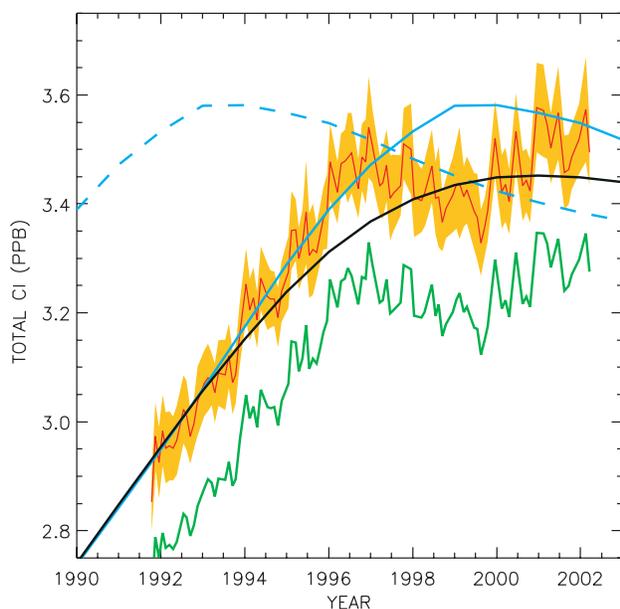


Figure 1-7. The time evolution of monthly mean HCl at altitudes of 54-56 km between 70°N and 70°S as measured by HALOE (green line: an update of Anderson et al., 2000). From this HCl record, total inorganic chlorine (Cl_y) mixing ratios at 55 km (red line) and their ± 1 standard deviations (orange shading) were derived using weighted contributions at 55 km altitude from all important source gases as determined from NCAR 2-D model calculations (Brasseur et al., 1990). Also shown are (i) CCl_y at Earth's surface based on the Ab scenario in Madronich and Velders et al. (1999) (dashed blue line), (ii) this surface result lagged by 6 years (solid blue line), and (iii) this lagged CCl_y convolved with a 3-yr-wide "age spectrum" (black line: an update of Waugh et al., 2001).

to CBr_y was 0.7 ppt in 1978, 6.7 ppt in 1996, and 7.7 ppt in 2000, and was increasing at $0.2 \text{ ppt Br yr}^{-1}$ in 2000 (Table 1-1; Figure 1-8).

Shorter-lived gases with predominantly natural sources, such as bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2), also add to the bromine burden of the atmosphere. Atmospheric measurements indicate between 1 and 3 ppt of organic bromine is present near the tropopause in the form of these gases (Shauffler et al., 1998; Pfeilsticker et al., 2000). Although the precise amount of organic plus inorganic bromine delivered to the stratosphere by these short-lived gases is uncertain (see Chapter 2), we estimate that in 2000 methyl bromide accounted for about 50% of CBr_y , and the halons accounted for about 40% of CBr_y .

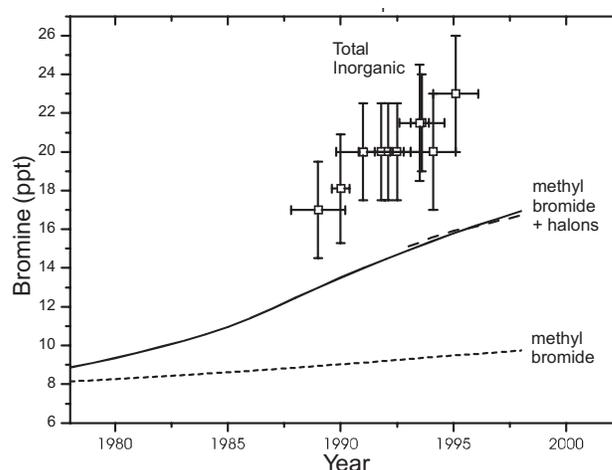


Figure 1-8. Past measured trends for bromine in the troposphere (lines) and stratosphere (points): global tropospheric bromine from methyl bromide as measured in ambient air and firn air (short dashed line: Khalil et al., 1993; Butler et al., 1999; Sturges et al., 2001a); global tropospheric bromine from the sum of methyl bromide plus halons as measured in ambient air, archived air, and firn air (solid line: Butler et al., 1999; Fraser et al., 1999; Sturges et al., 2001a), or as derived from firn-air and global flask samples (long-dashed line: Butler et al., 1998); and total inorganic bromine derived from stratospheric measurements of BrO and photochemical modeling that accounts for BrO/Br_y partitioning (open squares: Harder et al., 2000; Fitzenberger et al., 2000; Pfeilsticker et al., 2000). The years indicated on the abscissa are sampling times for tropospheric data. For stratospheric data, the date corresponds to when that air was last in the troposphere (i.e., sampling date minus mean time in stratosphere).

1.2.4.2 TOTAL INORGANIC BROMINE IN THE STRATOSPHERE

The burden and trend of inorganic bromine (Br_y) in the stratosphere can be estimated indirectly from measurements of organic source gases in the stratosphere (Shauffler et al., 1998; Wamsley et al., 1998) and from stratospheric bromine monoxide (BrO) measurements and calculated BrO/Br_y partitioning (Harder et al., 2000; Pfeilsticker et al., 2000; Sinnhuber et al., 2002). In stratospheric air in which most organic source gases had become oxidized, Br_y was estimated in early 1999 to be $18.4 (+1.8/-1.5)$ ppt from organic precursor measurements and 21.5 ± 3.0 ppt from coincident BrO measurements and photochemical modeling (Pfeilsticker et al.,

SOURCE GASES

2000; measurements were made at 25 km in air inferred to have a 5.6-yr mean age). Lower in the stratosphere, Br_y is a much smaller fraction of total bromine; these same investigators estimated Br_y to be 1.5 ppt in air just above the local Arctic tropopause (about 9.5 km).

1.2.4.3 STRATOSPHERIC BROMINE COMPARED WITH TROPOSPHERIC BROMINE

Spectrometric BrO measurements allow for estimates of total stratospheric Br_y . These measurements suggest an increase in Br_y over time and a stratospheric burden that is 4 to 6 ppt higher than indicated by the tropospheric burdens of halons and methyl bromide alone (Figure 1-8; an update of Pfeilsticker et al., 2000). Measurements of long- and short-lived gases at the tropopause and throughout the stratosphere suggest that an additional 1 to 3 ppt of bromine reaches the stratosphere in the form of organic short-lived gases, such as dibromomethane and bromoform (Schauffler et al., 1998; Wamsley et al., 1998; Pfeilsticker et al., 2000). This additional bromine does not appear to account for all the BrO measured, however. The remaining difference may suggest the presence of unmeasured, brominated organic gases reaching the stratosphere, or an influx of inorganic bromine into the stratosphere (see Chapter 2), or calibration errors either in the measurement of BrO or the organic source gases (Fitzenberger et al., 2000).

1.2.5 Effective Equivalent Chlorine and Effective Equivalent Stratospheric Chlorine

The net effect of changes in both atmospheric chlorine and bromine can be gauged roughly by computing effective equivalent chlorine (EECI) and effective equivalent stratospheric chlorine (EESC) from ground-based measurements of halocarbons (Prather and Watson, 1990; Daniel et al., 1995; Montzka et al., 1996a, 1999; WMO, 1999). EECI is calculated with ground-based halocarbon measurements, consideration of the enhanced efficiency of bromine to deplete stratospheric ozone (a factor of 45 used here; see discussion of α in Section 1.4.4), and consideration of the relative rates at which halocarbons decompose and release their halogen into the stratosphere. Ground-based measurement networks of the most abundant ODSs indicate that total ozone-depleting halogen measured in the troposphere peaked in 1992-1994 (Figure 1-9; Montzka et al., 1996a; Cunnold et al., 1997). Updated observations show that EECI in tropospheric air declined from 1995 through 2000 at a mean rate of about 1.2% yr^{-1} , or 24 ppt EECI yr^{-1} . As of mid-2000, EECI was about 5% below the peak that was observed in 1992-1994.

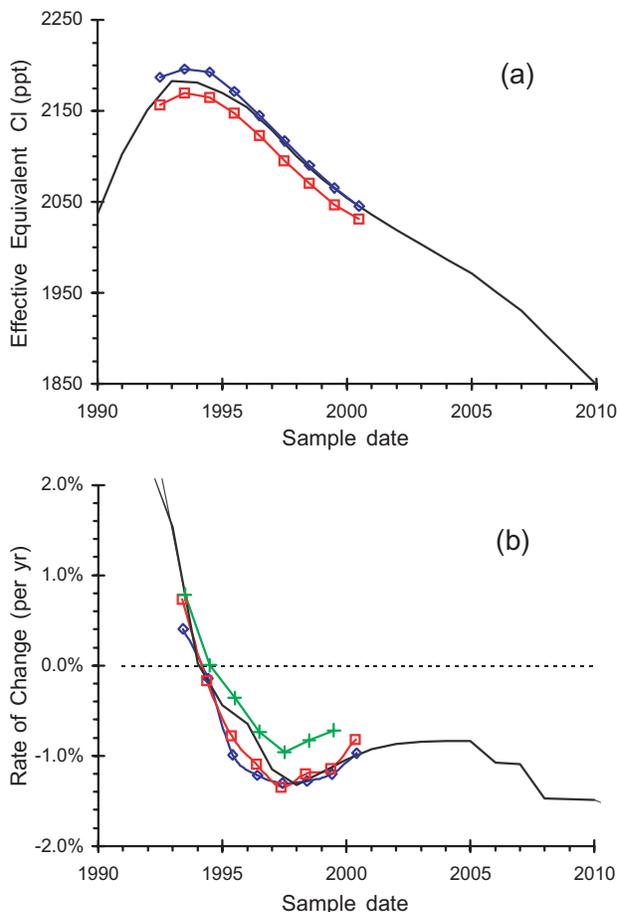


Figure 1-9. Burden and trends in aggregate tropospheric Cl plus Br from purely anthropogenic halocarbons expressed as effective equivalent chlorine. (a) Effective equivalent chlorine estimated from ground-based measurements of the major CFCs, methyl chloroform, carbon tetrachloride, Halon-1211, Halon-1301, and HCFCs (blue line with diamonds: Montzka et al., 1999; red line with squares: Prinn et al., 2000), and from the same gases as in scenario Ab (thin smooth line). The time scale on the x-axis refers to the date tropospheric air was sampled; to convert to effective equivalent stratospheric chlorine (EESC), add approximately 3 years to these dates. (b) The rate of change in effective equivalent chlorine as measured by [AGAGE + CMDL halon] measurements (red squares); CMDL measurements only (blue diamonds); [AGAGE + UEA halon] measurements (green plus symbols: halon data from Fraser et al., 1999); and in scenario Ab (thin solid line). Rates of change correspond to the 12-month difference over the previous 12 months. In both panels, total bromine was multiplied by 45, and the absolute fractional release assumed for CFC-11 was 0.8 (see Section 1.4.4).

Smaller declines and slower rates of decline are inferred when halon measurements by UEA at Cape Grim are considered (Figure 1-9; update of Fraser et al., 1999).

Although decreases observed for methyl chloroform are the primary reason for the turnover in EECl, the influence of methyl chloroform on EECl is diminishing. Furthermore, the increases still observed for CFC-12 and halons are slowing the decline of EECl (Fraser et al., 1999; Montzka et al., 1999). As a result of these influences, EECl decreased in 2000 at a rate that was only about two-thirds of the rate 3 to 4 years earlier (Figure 1-9). As the influence of methyl chloroform continues to lessen, a sustained decrease in EECl is assured only if trends for other halocarbons decrease further or become more negative (Montzka et al., 1999; see also Section 1.8).

Whereas EECl reflects the time evolution of equivalent effective halogen only in the troposphere, EESC provides an estimate of that burden in the stratosphere. EESC is derived by simply adding a 3-year time lag to EECl (see Section 1.8). Although EESC provides a useful measure to gauge the combined influence of tropospheric chlorine and bromine trends on stratospheric ozone-depleting halogen, it has important limitations. First, stratospheric halocarbon abundances lag tropospheric abundances by a few months to 6 years, depending upon location. Despite this range, a lag of 3 years is generally used in the calculation of EESC to approximate the mean transport time for air from the surface to the lower-mid stratosphere, which is where most ozone depletion has been observed. The 3 years is typical of the average age of air (time since air was in the troposphere; see Section 1.4.3) in these regions. Second, stratospheric halocarbon burdens are not determined by tropospheric burdens at a single time in the past. They instead represent a mean of tropospheric burdens from a range of earlier years (Hall and Plumb, 1994); this can result in errors with this simple technique especially when atmospheric mixing ratios are changing nonlinearly. Finally, Prather (1997) pointed out that the rate at which halogens are removed from the stratosphere has its own time scale in addition to the lag time associated with transport of halocarbons into the stratosphere. For short-lived halocarbons such as methyl bromide, whose tropospheric abundance could decrease rapidly relative to the rates at which air is transported into or out of the stratosphere, the decay of stratospheric inorganic halogen resulting from a rapid drop in tropospheric burden would be delayed and would not be well approximated by a single lag time. This effect is less important for most chlorinated ODSs because they have atmospheric lifetimes that are long relative to these transport rates.

Trends for EECl and EESC depend upon our understanding of the equivalency factor for bromine (α),

which varies over different latitudes and altitudes and is weighted by the distribution of stratospheric ozone (Daniel et al., 1999; see also Section 1.4.4). Although 45 represents a globally-weighted mean for α , higher estimates for this equivalency factor would suggest smaller decreases for EECl during years in which bromine continued to increase.

1.2.6 Fluorine in the Stratosphere

Measurements of hydrogen fluoride (HF) and carbonyl fluoride (COF_2), which are primarily concentrated in the stratosphere (Zander et al., 1992), provide an estimate of changes in the total fluorine burden of the atmosphere (Sen et al., 1996). Although fluorine does not catalytically destroy stratospheric ozone, trends in F_y^* (defined here as $F_y^* = [\text{HF}] + 2 \times [\text{COF}_2]$) have provided an independent measure of changes in the abundance of ozone-depleting substances (Gunson et al., 1994; Anderson et al., 2000).

Since the previous Assessment (WMO, 1999), long-term investigations of HF and COF_2 have continued, both from the ground and from space. Related Jungfraujoch results show a steady increase in column F_y^* until the mid-1990s, and a slower rate of increase afterward (Figure 1-10; updates to Mahieu et al., 2000 and Mélen et al., 1998). Two-dimensional (2-D) model calculations that include atmospheric histories for the most abundant, anthropogenic F-containing gases (CFC-12, CFC-11, CFC-113, HCFC-22, Halon-1211, and Halon-1301, which all are important ODSs) reproduce the measured trends in F_y^* above the Jungfraujoch station reasonably well (Figure 1-10; Chipperfield et al., 1997). This consistency provides further evidence that anthropogenic ODSs undergo photochemical degradation in the stratosphere and are responsible for the large increases in stratospheric chlorine and fluorine observed during the past 20 years or more. Similar conclusions have been drawn from analyses of the near-global mean HF measurements at 55 km from HALOE (Anderson et al., 2000) and from ATMOS measurements of individual F-containing gases between 1985 and 1994 over the altitude range of 8 to 60 km (Irion et al., 2002).

1.3 HALOCARBON SOURCES ESTIMATED FROM INDUSTRIAL PRODUCTION

The combination of halocarbon production data from both the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS, 2001) and the United Nations Environment Programme (UNEP, 2002) have allowed for the first time a rigorous estimate of total global production and consumption of ozone-depleting halocar-

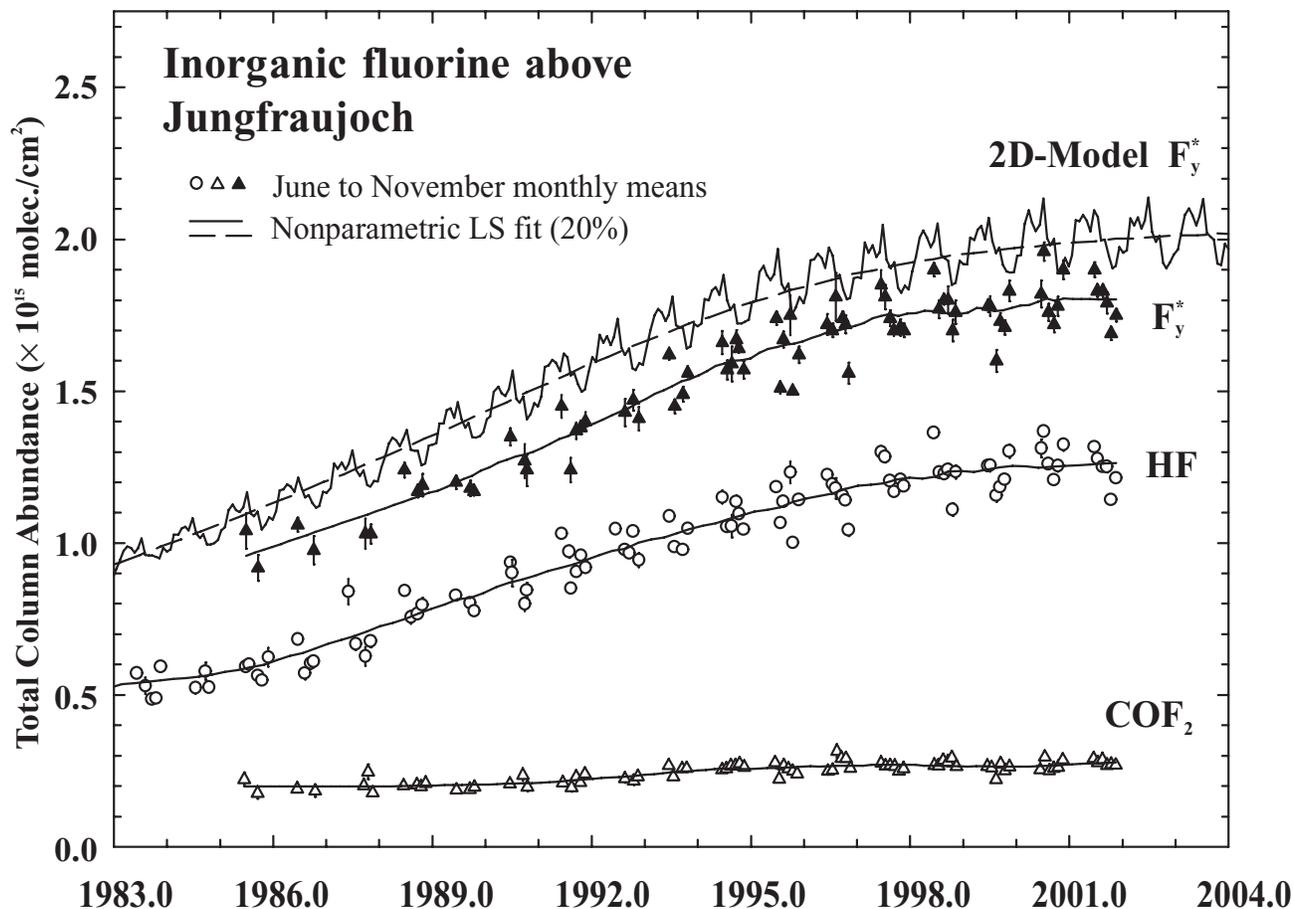


Figure 1-10. Time series of monthly mean vertical column abundances of HF (open circles: update from Mahieu et al., 2000); COF_2 (open triangles: update from Mélen et al., 1998); and their weighted sum, F_y^* (filled triangles; where $F_y^* = [\text{HF}] + 2 \times [\text{COF}_2]$) derived from observations at the Jungfraujoch (46.5°N) between 1983 and 2001. Only measurements from June to November are shown to avoid the significant variability observed during winter and spring. The thick lines through the individual datasets represent nonparametric least-squares fits with 20% weighting. Also shown is column F_y^* above the Jungfraujoch calculated with a two-dimensional model (Chipperfield et al., 1997). The model-calculated F_y^* minima occur in late summer/fall. The 10-12% high bias in the model calculations compared with the summer/fall observations is believed to arise in part from systematic uncertainties in the meridional transport of the 2-D model (see discussion in Chapter 4). Long-term column HF measurements above Kitt Peak indicate rates of change similar to those observed at the Jungfraujoch, but are not shown here (Rinsland et al., 2002b).

bons. Although the UNEP data provide more complete geographical coverage than AFEAS, they are not audited. The audited AFEAS data provide discrimination of production data by individual gases for all Parties other than China, India, and Korea. For this report, the aggregated additional production in these countries was subdivided into individual compounds as follows: HCFCs were treated as being produced in the same ratio as in the AFEAS data, and only CFC-11 and -12 contributed to the additional production of CFCs, consistent with there being little production of CFC-113 outside of the companies reporting to AFEAS (personal communication, M.R.

Harris, World Bank, 1999). In the case of methyl chloroform, global production data were derived from a similar combination of an industrial database (McCulloch and Midgley, 2001) and data in UNEP (2002). For the halons, global production data were derived from Fraser et al. (1999), updates to UNEP (1999), UNEP (2002), and also from reports to the Parties on the Multilateral Fund, for example, as described in Bingfeng et al. (2000).

None of these substances is emitted immediately after it is produced; emissions occur over a period during and after use that varies depending upon the application. In some cases, notably where the substance is used as a sol-

vent, emissions are prompt and can be well characterized in quantity and timing. Since the previous Assessment (WMO, 1999), emission functions that relate the quantities of fluorocarbons in use to the quantities released into the atmosphere have been intensively re-examined and, in some cases, revised (Ashford, 2000). In the case of HCFC-142b this has resulted in a significant change in the emission function and the calculated quantities emitted (AFEAS, 2001). It is also apparent that containment of most CFCs and HCFCs began to improve in the early 1990s. For example, emissions of CFC-11 from foam blowing showed a sharp reduction after about 1992 (McCulloch et al., 2001), and these changes are included in the revised release functions. Emissions from some refrigeration applications have been reduced in recent years (UNEP, 1998a; Calm, 1999), but these systems represent only a small fraction of total emissions from refrigeration. A single emission function for refrigeration has been used for more than 30 years (McCulloch et al., 2001, 2002).

Ongoing work by the Technology and Economic Assessment Panel (TEAP) has also allowed for independent estimates of halons, as discussed below.

1.3.1 CFCs and HCFCs

For substances used in refrigeration, there is an initial loss of between 5% (CFC-12) and 35% (HCFC-22), and complete emission within 10 years for the average system (Gamlen et al., 1986; Midgley and Fisher, 1993; McCulloch et al., 2002). This is consistent with the average linear loss rate of 11% yr⁻¹ described by Baker (1999). However, the actual distribution of emissions is approximately normal around 4.5 ± 2 years.

1.3.2 Halons

Halons are primarily used as fire extinguishing agents, although Halon-1301 also received minor use as a cold-temperature refrigerant. UNEP (1998b) suggests that production data as reported to the UNEP Ozone Secretariat is accurate. Two estimates of emissions for Halon-1211 and -1301 have been made using similar production data (Fraser et al., 1999; updated UNEP, 1999), but since very different emission functions were used, markedly different emission rates were obtained (see Section 1.6). Further, the extent of inadvertent halon emissions from some production facilities has yet to be characterized but may be substantial (UNEP, 1999).

1.3.3 Carbon Tetrachloride (CCl₄)

The principal identified use of carbon tetrachloride is as feedstock for the production of CFC-11 and -12, and

from this process releases to the atmosphere arise only from fugitive losses. Large discrepancies existed in UNEP consumption data for past years owing to confusion over reporting procedures, and although these have been addressed by TEAP (UNEP, 1998b), there may still be significant omissions and unrecorded sources (see Section 1.6). TEAP suggests emissions of 41(+50%, -25%) Gg from total production of 203 Gg in 1996 (UNEP, 1998b), but, as discussed in Section 1.6, this is only about half of the emissions necessary to account for observed burdens and trends in that year given the updated lifetime estimate of 26 years (see Section 1.4).

1.3.4 Methyl Chloroform (CH₃CCl₃)

Industrial production and release to the atmosphere of methyl chloroform declined dramatically in the 1990s (McCulloch and Midgley, 2001; UNEP, 2002). Global anthropogenic emissions in 1999-2000 were estimated at about 20 Gg yr⁻¹, or only 3% of the emissions estimated for 1989-1990, the peak emission years. Declines in emission closely follow declines in production because methyl chloroform was used predominantly in applications where releases occurred soon after sales.

Firn results (Butler et al., 1999; Sturrock et al., 2002) suggest mixing ratios in the early 1990s, before industrial production began, of less than 4 ppt and confirm that use by industry was the main source of atmospheric methyl chloroform.

Reports have suggested that small amounts of methyl chloroform are emitted from biomass burning. Upper limits quoted in an early study (Rudolph et al., 1995) have since been revised downward with additional laboratory work and suggest emissions may be on the order of 2-10 Gg yr⁻¹ from burning (Rudolph et al., 2000). Emissions of this magnitude would sustain global mixing ratios of 0.5-2 ppt, consistent with inferences from the analysis of firn air.

1.4 HALOCARBON LIFETIMES, OZONE DEPLETION POTENTIALS, AND GLOBAL WARMING POTENTIALS

1.4.1 Introduction

Halocarbon sinks chemically transform or physically remove halogen-containing source species from the atmosphere after release. Known atmospheric sinks for halocarbon source gases include photolysis, reaction with hydroxyl radical (OH) in both the troposphere and stratosphere, reaction with electronically excited atomic oxygen (O(¹D)) and atomic chlorine (Cl) chiefly in the strato-

SOURCE GASES

sphere, uptake in oceanic surface waters through chemical and biological degradation processes, biological degradation in soils, and possibly surface reactions on minerals. Not all halocarbon source gases become degraded by all of these sink processes. The quantitative determinations of trace gas sink strengths are of interest because the sinks control both the atmospheric lifetimes and the location of halogen release from source gases.

The important sink processes for atmospheric lifetime are those that have significant strength on a mass or molecule basis, that is, where loss frequency and atmospheric abundance are co-located. A simple definition of lifetime is the sum of the integrals over the entire atmosphere of the product of the first-order sink process frequencies (the local instantaneous lifetimes) and the normalized source gas mass or concentration distribution.

1.4.2 Lifetimes

For a given halocarbon, each relevant sink process contributes to the additive first-order total loss frequency, L , which is variable in space and time. A local halocarbon lifetime, τ_{local} , can be defined as the inverse of L evaluated at a point in space and time:

$$\tau_{\text{local}} = \frac{1}{L(x, y, z, t)} \quad (1-1)$$

For consideration of global effects of the halocarbon, L must be integrated globally, and the integral must be weighted by the distribution of the halocarbon on which the sink processes act. If we consider a normalized halocarbon distribution $n(x, y, z, t)$, a global instantaneous lifetime can be defined as

$$\tau_{\text{global}} = \frac{\int dV n(V, t) (=1)}{\int dV L(V, t) n(V, t)} \quad (1-2)$$

where V is an atmospheric volume element. This expression can be averaged over a year to determine the global, annually averaged lifetime. Because the total loss frequency L is the sum of the individual sink process frequencies, τ_{global} can also be expressed in terms of process lifetimes; for example,

$$\tau_{\text{global}} = \left[\frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{ocean}}} + \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{\text{other processes}}} \right]^{-1} \quad (1-3)$$

Note that in considering lifetime with respect to individual sink processes, which may be defined or analyzed over limited domains, the associated burden (the numerator in Equation (1-2)), however, must always be

global and include all communicating reservoirs. When the halocarbon distribution is time invariant, where emissions, sinks, and atmospheric transport are in long-term balance, the halocarbon burden $B(t)$ can be defined by

$$\frac{dB(t)}{dt} = E(t) - \frac{B(t)}{\tau_{\text{global}}} \quad (1-4)$$

and the lifetime τ_{global} becomes a scale factor relating the halocarbon emission rate $E(t)$ (or equivalently the sink rate) to the atmospheric burden. This steady-state lifetime is also formally equivalent to the scale factor relating the time-integrated atmospheric burden to a release of halocarbon at a single point in time (Prather, 1996). For source compounds that do not persist long enough to become well mixed in the troposphere (here assumed for gases with $\tau < 0.5$ years), distributions are strongly dependent on the pattern of emissions. Consequently, the concept of a single global lifetime, ODP, or GWP becomes inappropriate for such short-lived gases (see Chapter 2). In this chapter, only local lifetimes are reported for short-lived gases (Table 1-3), and these lifetimes are not derived from any actual steady-state global emission/distribution patterns. (GWPs for these gases are not reported in Table 1-6 because of these concerns.) Finally, a discussion of the ODP concept for short-lived gases is addressed in Chapter 2.

WMO (1999) and IPCC (2001) include detailed discussions of the various specific techniques for estimating steady-state and non-steady-state global lifetimes, to which the reader is referred. The techniques fall into four general categories: (1) lifetimes derived from model-calculated distributions and sink loss frequencies, (2) lifetimes inferred by inverse methods from direct observations of halocarbon abundance with high precision and accuracy over multiyear periods and requiring varying degrees of knowledge about actual emissions, (3) lifetimes determined relative to a reference species with an independently derived lifetime through observations of species correlations or knowledge of relative kinetic rate parameters, and (4) lifetimes determined from some combination of the above three techniques, where the total lifetime is determined as the combination of individual process lifetimes.

Important advancements have been made in our understanding of halocarbon lifetimes since WMO (1999). Those relate to improvements in understanding the lifetime of methyl chloroform and in choosing a globally representative temperature that allows better estimates of lifetimes of other gases destroyed by OH.

Recently reported analyses of methyl chloroform lifetime based on observations from global sampling net-

works over multiyear periods (Montzka et al., 2000; Prinn et al., 2000, 2001) suggest a slightly longer central value than previous World Meteorological Organization (WMO) and Intergovernmental Panel on Climate Change (IPCC) reports (Kurylo and Rodríguez et al., 1999; Prather and Ehhalt et al., 2001). Additionally, stratospheric in situ correlation measurements (Volk et al., 1997) derive a somewhat shorter stratospheric lifetime than was adopted in these Assessments. Because CH_3CCl_3 acts as the reference compound for the relative determination of lifetime with respect to tropospheric OH oxidation for the large suite of hydrogenated halocarbons, changes in CH_3CCl_3 lifetime need to be carefully considered. Equation (1-3) is employed to determine the value of τ_{OH} for CH_3CCl_3 (here derived to be 6.1 years, see below), where τ_{global} (= 5.0 years) is inferred from direct observations of CH_3CCl_3 and estimates of emissions; $\tau_{\text{photolysis}}$ (= 38-41 years) arises from loss in the stratosphere and is inferred from observed stratospheric correlations among CH_3CCl_3 , CFC-11, and the stratospheric age of the air mass observed; τ_{ocean} (= 94 years) is derived from a model of the oceanic loss process; and $\tau_{\text{other processes}}$ is taken to be zero.

The total atmospheric lifetime value adopted here of 5.0 years for methyl chloroform at steady state (i.e., unchanging distribution or balanced emission and loss) lies between the mean lifetimes inferred from observations for non-steady-state periods of 5.2 (+0.2/-0.3) years (Montzka et al., 2000) and 4.9 (+0.6/-0.5) years (Prinn et al., 2001) and below the observationally derived upper limit of 5.5 years (Montzka et al., 2000). Note that the difference between these observational lifetimes is not ascribed to simple uncertainties in calibration accuracy or measurement precision. The Prinn et al. (2001) value pertains to the average global OH during 1978-2000, whereas the Montzka et al. (2000) value refers specifically to 1998-1999, a time period for which Prinn et al. (2001) suggest that global OH fell below the long-term average, producing a longer instantaneous lifetime.

The oceanic sink lifetime of methyl chloroform has been reassessed recently based on a high-resolution model of ocean processes and surface mixing, and a value of 94 years was calculated (Yvon-Lewis and Butler, 2002), similar to the lifetime adopted in the previous Assessment (WMO, 1999). Given the above-mentioned revisions, the previously adopted process OH lifetime of 5.7 years would require an unrealistically long stratospheric-loss lifetime (much greater than 45 years), where recent reports indicate even shorter values (≤ 40 years). A longer lifetime of 6.1 years with respect to tropospheric hydroxyl radical reaction is consistent with stratospheric-loss lifetimes of 38 to 41 years. This range of stratospheric-loss lifetime lies between lower values inferred from tracer-tracer cor-

relations (Volk et al., 1997; Schauffler et al., 2002) and higher values calculated in multidimensional models (WMO, 1999). The general effect of this updated recommendation is to lengthen lifetimes of hydrogen-containing halocarbons and methane by about 7% relative to the two most recent Assessment reports, and to increase estimates for their ODP and GWP values by a similar amount.

Spivakovsky et al. (2000) have computed a global climatological distribution of tropospheric OH based on observed distributions of the OH-controlling quantities. Using this OH distribution and assuming a well-mixed distribution for the OH reaction partner, they show that selecting a temperature of 272 K to evaluate a tropospheric average OH rate constant produces a good fit over a wide range of activation energies in the Arrhenius rate constant expression. As in IPCC (2001), this value is adopted here in calculating lifetimes by reference to CH_3CCl_3 in Table 1-3. WMO (1999) used an earlier 277 K estimate for this value. The OH reaction rate constants used in generating the Table 1-3 lifetimes are the new recommendations of the NASA Panel for Data Evaluation (Sander et al., 2002).

The global lifetime for Halon-1211 (CBrClF_2) has been reassessed. This gas is destroyed exclusively by photolysis in both the troposphere and stratosphere, which makes it a somewhat special case among halogen source gases. Past lifetime recommendations that depend on cross section data and model calculations include 12-18 years (WMO, 1989), 18.5-20.1 years (WMO, 1991), 9.3-28.2 years (Kaye et al., 1994), and 20 years (WMO, 1995). The Halon-1211 lifetime has also been inferred from a comparison between observed atmospheric burdens and emission histories derived from halon production magnitudes. Uncertainty in both the atmospheric measurements and available release histories (Fraser et al., 1999; an update to UNEP, 1999) do not constrain these estimates to better than 11-30 years (see Section 1.6). Finally, the stratospheric component of the Halon-1211 lifetime has been inferred from correlating stratospheric observations of this halon to age of stratospheric air, nitrous oxide (N_2O), and CFC-11 (e.g., Volk et al., 1997). This stratospheric lifetime is difficult to combine appropriately with modeled estimates of tropospheric loss, although the available estimates suggest a global Halon-1211 lifetime of about 14 years. Because of the uncertainties surrounding observational-based lifetime estimates, the recommendation for the total steady-state lifetime of Halon-1211 is updated here to 16 years based primarily on reported model-calculated values known to include the tail of the Halon-1211 absorption between 300 and 400 nm (Burkholder et al., 1991; Fraser et al., 1999). Clearly additional laboratory, observational, and modeling studies will be needed to reduce the uncertainties in this lifetime.

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Table 1-3. Halogenated trace gas lifetimes.

Industrial Designation or Common Name	Chemical Formula	Lifetime (years)	Notes
Halogen-substituted methanes			
HFC-41	CH ₃ F	2.4	1
HFC-32	CH ₂ F ₂	4.9	1
HFC-23	CHF ₃	270	1
FC-14 (carbon tetrafluoride)	CF ₄	50 000	2
Methyl chloride	CH ₃ Cl	1.3	1, 3
Dichloromethane	CH ₂ Cl ₂	0.38	15, 16
Chloroform	CHCl ₃	0.41	15, 16
Carbon tetrachloride	CCl ₄	26	5
HCFC-31	CH ₂ ClF	1.3	4
HCFC-22	CHClF ₂	12.0	1, 6
HCFC-21	CHCl ₂ F	1.7	1, 6
CFC-13	CClF ₃	640	2
CFC-12	CCl ₂ F ₂	100	2, 7
CFC-11	CCl ₃ F	45	2, 7
Methyl bromide	CH ₃ Br	0.7	3
Dibromomethane	CH ₂ Br ₂	0.33	8, 15, 16
Bromoform	CHBr ₃	0.07	8, 15, 16
Bromodifluoromethane	CHBrF ₂	5.8	4
Bromochloromethane	CH ₂ BrCl	0.37	8, 15, 16
Bromodichloromethane	CHBrCl ₂	0.21	7, 15, 1
Dibromochloromethane	CHBr ₂ Cl	0.19	7, 15, 16
Halon-1301	CBrF ₃	65	2, 7
Halon-1211	CBrClF ₂	16	9
Halon-1202	CBr ₂ F ₂	2.9	17
Methyl iodide	CH ₃ I	0.02	7, 15, 16
Diiodomethane	CH ₂ I ₂	Minutes	7, 15, 16
Chloriodomethane	CH ₂ ClI	Hours	7, 15, 16
Trifluoroiodomethane	CF ₃ I	<0.005	2, 15
Halogen-substituted ethanes			
HFC-161	CH ₃ CH ₂ F	0.21	2, 15
HFC-152	CH ₂ FCH ₂ F	0.60	2, 15
HFC-152a	CH ₃ CHF ₂	1.4	1, 6
HFC-143	CH ₂ FCHF ₂	3.5	1
HFC-143a	CH ₃ CF ₃	52	1
HFC-134	CHF ₂ CHF ₂	9.6	1
HFC-134a	CH ₂ FCF ₃	14.0	1, 6
HFC-125	CHF ₂ CF ₃	29	1, 6
FC-116 (perfluoroethane)	CF ₃ CF ₃	10 000	2
chloroethane	CH ₃ CH ₂ Cl	0.11	15
1,1 dichloroethane	CH ₂ ClCH ₂ Cl	0.19	10, 15
Methyl chloroform	CH ₃ CCl ₃	5.0	9

Table 1-3, continued.

Industrial Designation or Common Name	Chemical Formula	Lifetime (years)	Notes
HCFC-142b	CH ₃ CClF ₂	17.9	1, 6
HCFC-141b	CH ₃ CCl ₂ F	9.3	1, 6
HCFC-123	CHCl ₂ CF ₃	1.3	6, 11
HCFC-124	CHClF ₂ CF ₃	5.8	6, 11
CFC-113	CCl ₂ FCClF ₂	85	2
CFC-113a	CCl ₃ CF ₃	NA	NA
CFC-114	CClF ₂ CClF ₂	300	2
CFC-115	CClF ₂ CF ₃	1700	2
Halon-2402	CBrF ₂ CBrF ₂	20	17
Halogen-substituted propanes			
HFC-281ea	CH ₃ CHFCH ₃	0.06	15
HFC-263fb	CH ₃ CH ₂ CF ₃	1.6	2
HFC-245ca	CH ₂ FCF ₂ CHF ₂	6.2	1
HFC-245ea	CHF ₂ CHFCHF ₂	4.0	2
HFC-245eb	CH ₂ FCHF ₂ CF ₃	4.0	12
HFC-245fa	CHF ₂ CH ₂ CF ₃	7.6	1
HFC-236cb	CH ₂ FCF ₂ CF ₃	13.6	1
HFC-236ea	CHF ₂ CHF ₂ CF ₃	10.7	1
HFC-236fa	CF ₃ CH ₂ CF ₃	240	1
HFC-227ea	CF ₃ CHF ₂ CF ₃	34.2	1
FC-218 (perfluoropropane)	CF ₃ CF ₂ CF ₃	2600	2
n-propyl chloride	CH ₃ CH ₂ CH ₂ Cl	0.06	13, 15
HCFC-243cc	CH ₃ CF ₂ CFCl ₂	26.4	4
HCFC-225ca	CHCl ₂ CF ₂ CF ₃	1.9	11
HCFC-225cb	CHClF ₂ CF ₂ CClF ₂	5.8	11
n-propyl bromide	CH ₃ CH ₂ CH ₂ Br	0.04	15, 16
n-propyl iodide	CH ₃ CH ₂ CH ₂ I	0.003	7, 15, 16
isopropyl iodide	CH ₃ CHICH ₃	0.002	7, 15
Halogen-substituted higher alkanes			
HFC-365mfc	CH ₃ CF ₂ CH ₂ CF ₃	8.6	1
HFC-356mcf	CH ₂ FCH ₂ CF ₂ CF ₃	1.2	1
HFC-356mff	CF ₃ CH ₂ CH ₂ CF ₃	8.1	1
HFC-338pcc	CHF ₂ CF ₂ CF ₂ CHF ₂	12.3	1
FC-318 (perfluorocyclobutane)	c-C ₄ F ₈	3200	1
FC-31-10 (perfluorobutane)	C ₄ F ₁₀	2600	2
HFC-43-10mee	CF ₃ CHFCH ₂ CF ₂ CF ₃	15.9	1
HFC-458mfcf	CF ₃ CH ₂ CF ₂ CH ₂ CF ₃	23.2	1
FC-41-12 (perfluoropentane)	C ₅ F ₁₂	4100	2
HFC-55-10mcff	CF ₃ CF ₂ CH ₂ CH ₂ CF ₂ CF ₃	7.7	2
FC-51-14 (perfluorohexane)	C ₆ F ₁₄	3200	2

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Table 1-3, continued.

Industrial Designation or Common Name	Chemical Formula	Lifetime (years)	Notes
Fluorinated alcohols			
	CF ₃ CH ₂ OH	0.41	15
	CF ₃ CF ₂ CH ₂ OH	0.39	15
	(CF ₃) ₂ CHOH	2.0	4
Fluorinated ethers			
HFE-152a	CH ₃ OCHF ₂	1.6	1
HFE-143a	CH ₃ OCF ₃	4.3	1
HFE-134	CHF ₂ OCHF ₂	26	1
HFE-125	CHF ₂ OCF ₃	136	1
HFE-227ea	CF ₃ OCHF ₂ CF ₃	11	2
HFCE-235da2	CHF ₂ OCHClCF ₃	2.6	2
HFE-236ea2	CHF ₂ OCHF ₂ CF ₃	5.8	2
HFE-236fa	CF ₃ OCH ₂ CF ₃	3.7	2
HFE-245fa1	CHF ₂ CH ₂ OCF ₃	2.2	2
HFE-245fa2	CHF ₂ OCH ₂ CF ₃	4.9	1
HFE-245cb2	CH ₃ OCF ₂ CF ₃	5.1	4
HFE-254cb2	CH ₃ OCF ₂ CHF ₂	2.6	4
HFE-263fb2	CH ₃ OCH ₂ CF ₃	0.1	2
HFE-329mcc2	CF ₃ CF ₂ OCF ₂ CHF ₂	6.8	2
HFE-338mcf2	CF ₃ CF ₂ OCH ₂ CF ₃	4.3	2
HFE-347mcc3	CH ₃ OCF ₂ CF ₂ CF ₃	5.2	4
HFE-347mcf2	CF ₃ CF ₂ OCH ₂ CHF ₂	2.8	2
HFE-347pf3	CHF ₂ OCH ₂ CF ₂ CF ₃	5.9	4
HFE-347sy2	CF ₃ CF(OCH ₃)CF ₃	3.7	4
HFE-356mec3	CH ₃ OCF ₂ CHF ₂ CF ₃	0.94	2
HFE-356mff2	CF ₃ CH ₂ OCH ₂ CF ₃	0.4	15
HFE-356pcc3	CH ₃ OCF ₂ CF ₂ CHF ₂	0.93	2
HFE-356pcf3	CHF ₂ OCH ₂ CF ₂ CHF ₂	3.6	4
HFE-356pcf2	CHF ₂ CH ₂ OCF ₂ CHF ₂	2	2
HFE-365mcf3	CH ₃ OCH ₂ CF ₂ CF ₃	0.11	2, 15
HFE-374pc2 ^a	CH ₃ CH ₂ OCF ₂ CHF ₂	5	2
	CF ₃ CH(OCH ₃)CHF ₂	3.1	2
	(CF ₃) ₂ CFOCH ₃	3.4	2
HFE-7100	C ₄ F ₉ OCH ₃	5	2
HFE-7200	C ₄ F ₉ OC ₂ H ₅	0.77	2
H-Galden 1040x ^b	CHF ₂ OCF ₂ OCF ₂ CF ₂ OCHF ₂	6.3	2
HFE-236ca12	CHF ₂ OCF ₂ OCHF ₂	12.1	2
HFE-338pcc13	CHF ₂ OCF ₂ CF ₂ OCHF ₂	6.2	2
Other fluorinated species			
Trifluoromethylsulfurpentafluoride	SF ₅ CF ₃	800	18
Sulfur hexafluoride	SF ₆	3200	2

Table 1-3, continued.

Footnotes

For completeness, estimates for local lifetimes for some very short-lived ($\tau < 0.5$ years) species are included. As discussed in Chapter 2, the atmospheric lifetimes for these species (defined as the ratio of burden to emission; see Prather and Ehhalt et al., 2001) depend on the location and time of emission. Thus, these local lifetimes should not be used in estimation of semiempirical ODP, GWP, or EESC calculations for these gases.

Notes:

1. Global lifetime estimated from a process lifetime with respect to tropospheric OH calculated relative to 6.1 years for CH_3CCl_3 , assuming an average temperature of 272 K (Spivakovsky et al., 2000; Prather and Ehhalt et al., 2001); OH rate constants from Sander et al. (2002); and stratospheric loss lifetimes inferred from IPCC (2001).
2. Prather and Ehhalt et al. (2001) and Ramaswamy et al. (2001).
3. See Section 1.5 for further discussion related to methyl halide global lifetimes.
4. Lifetime calculated as in Note 1 except that no estimate of a stratospheric loss lifetime was available to include in the lifetime estimate listed. Hence this is an upper bound to the global lifetime estimate.
5. IPCC (2001) and including an oceanic loss term with 94-year lifetime observed in saturation data and ascribed to an unidentified process (Yvon-Lewis and Butler, 2002).
6. Including oceanic loss term from Yvon-Lewis and Butler (2002). The contribution of oceanic loss to the lifetime of HCFC-21, HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HFC-125, and HFC-152a is small; for HFC-134a and HCFC-142b it is negligibly small at the reported precision.
7. WMO (1999).
8. Lifetimes listed include local tropospheric photolysis lifetimes from Table 2-9 in Kurylo and Rodríguez et al. (1999). Consideration of only tropospheric OH loss results in local lifetimes of 0.34 years for CH_2Br_2 , 0.21 years for CHBr_3 , and 0.37 years for CH_2BrCl .
9. See Section 1.4 text for discussion.
10. OH rate constant from Qui et al. (1992).
11. Lifetime calculated as in Note 1, but with stratospheric loss from Naik et al. (2000).
12. Lifetime calculated as in Note 1, but with OH rate constant and stratospheric loss from Naik et al. (2000).
13. Markert and Nielsen (1992).
14. OH rate constant from DeMore and Bayes (1999).
15. The values estimated correspond to local lifetimes in the free troposphere. For species that react with OH, the process lifetime due to OH reaction is calculated using the rate constant at 275 K (for lifetimes greater than 10 days) or 300 K (for lifetimes less than 10 days) and OH concentration of 1×10^6 molec cm^{-3} . These should not be used in estimating ODP, GWP, or EESC because the atmospheric burden for these short-lived gases ($\tau < 0.5$ years) depends on the location and time of emissions.
16. See Chapter 2.
17. From the 2-D model calculation in Fraser et al. (1999).
18. Takahashi et al. (2002).

^a Referred to as HFE-374pcf2 in past Assessments.

^b Also known as HFE-43-10pccc124.

Previous lifetime estimates of carbon tetrachloride were derived from observations and modeling of photolytic loss rates in the stratosphere (Volk et al., 1997; Prinn and Zander et al., 1999). Reports of widespread observations of undersaturation of carbon tetrachloride in the ocean (Huhn et al., 2001; Wallace et al., 1994) suggest an additional, significant loss for this gas (Yvon-Lewis and Butler, 2002). When combined with the other loss processes, a revised global lifetime of 26 (17-36) years is now calculated for this gas (Yvon-Lewis and Butler, 2002).

1.4.3 Fractional Release Factors

In considering the effect of halogen source gases on ozone, it is first necessary to determine the composition of tropospheric air entering the stratosphere, mostly through the tropical tropopause. For compounds with lifetimes measured in years, the amount of halogen entering the stratosphere for a specific level of emission is

inversely related to the lifetime at steady state. Once a halogen source gas is in the stratosphere, release of a halogen atom from the source gas through photolysis or chemical reaction is a function of stratospheric local lifetime or loss frequency and differs greatly from compound to compound. More complete release of the halogen atom catalyst in the stratosphere produces a greater extent of local photochemical loss of ozone, for a given source gas or in comparing source gases, all else being equal.

A point measurement of a given halogen source molecule in the stratosphere can be recast as a fractional release (FR), defined as

$$\text{FR} = \frac{\rho_{\text{entry}} - \rho_{\text{point}}}{\rho_{\text{entry}}} \quad (1-5)$$

where ρ is the source compound mixing ratio or mole frac-

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tion. Observations of halogen source compounds at high spatial resolution in the stratosphere, chiefly by in situ techniques, show a compact relationship when plotted as a scatter correlation of fractional release of compound x to that of compound y . Identifying compound y as CFC-11 produces the fractional release factor that is used in the semiempirical determination of ODPs. It is essentially a measure of the local release or availability of the inorganic halogen compounds that actually produce the ozone depletion, relative point by point to CFC-11. These relative fractional release factors are used in the calculation of ODP, EECl, and EESC.

Although the correlations are compact, they are typically not simply linear, because local loss frequencies differ from compound to compound. Conceptually, the fractional release factor could be globally integrated, weighted by the local ozone loss. In practice, Schauffler et al. (1999) suggest the use of a restricted range of the correlation representing mid-high latitudes, where the greatest loss of ozone occurs. Schauffler et al. (2002) report fractional release factors for three ranges of stratospheric age of air, G , determined from N_2O abundance observed during the Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE), Stratospheric Tracers of Atmospheric Transport (STRAT), and Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) aircraft campaigns. High values of N_2O , near those in the troposphere, are associated with air that has recently entered the stratosphere, whereas low N_2O values are indicative of air that has cycled through the stratosphere by the mean circulation. The mean halocarbon fractional release values associated with ages of 2.0-4.5 years are appropriate for the midlatitude middle stratosphere. Earlier studies (Daniel et al., 1995) suggest a reference CFC-11 fractional release value of 0.8 for air that had passed through the mean circulation. Schauffler et al. (2002) relate this to older stratospheric air ($G = 4.5$ years). For 3.5-yr-old air, they indicate a CFC-11 fractional release of 0.55. Relative fractional release values derived from stratospheric observations of air of intermediate ages are given in Table 1-4. Because these are relative quantities, they are sensitive to nonlinearities in the slopes of correlation plots of release against age of air, but less sensitive to the absolute CFC-11 reference value.

Models and a semiempirical framework have been used to estimate fractional release factors for unmeasured or currently nonexistent atmospheric source gases (Solomon et al., 1992). Models predict ozone loss explicitly, however, so it is generally more straightforward to integrate the modeled ozone loss and calculated ODP directly as opposed to using a modeled release factor in

the semiempirical approach. The fractional release values for HCFC-141b and -142b used here and in past Assessments (Table 1-4) are based upon a semiempirical analysis of measured stratospheric profiles for methane and other gases (Solomon et al., 1992). A recent analysis of HCFC observations in the stratosphere, however, suggests the possibility for much smaller (by factors of 3 to 5) fractional release values and ODPs for HCFC-141b and -142b (Schauffler et al., 2002; Tables 1-4 and 1-5). Such low estimates are difficult to reconcile with the earlier estimates, given that only comparatively small refinements have been noted for reaction rate constants and other relevant model parameters since the original calculations were performed. Without additional research, changes to ODPs calculated for these HCFCs cannot be recommended at this time.

1.4.4 Ozone Depletion Potential

The Ozone Depletion Potential (ODP) is an integrative quantity, distinct for each halocarbon source species, that represents the extent of ozone depletion in the stratosphere expected from the halocarbon on a mass-for-mass basis relative to CFC-11. The formal definition of ODP is the ratio of integrated perturbations to total ozone, for a differential mass emission of a particular compound relative to an equal emission of CFC-11. An extensive discussion of the details of the ODP calculation is given in WMO (1995).

Solomon and coworkers (Solomon et al., 1992; WMO, 1995) introduced a semiempirical ODP formulation that takes advantage of the relative nature of the ODP definition to remove the requirement for explicit representations of ozone-controlling photochemistry in the context of chemistry-transport models. The quantities required are physical properties of the halocarbons, their lifetimes, a factor representing the distribution of inorganic halogen release in the stratosphere obtained from observation, and, in the case of bromine and iodine, an analysis of the catalytic efficiency of ozone destruction relative to chlorine, derived from knowledge of the kinetic parameters of the partitioning of the halogen radical families. For long-lived gases that are well mixed in the troposphere, the semiempirical ODP definition is

$$\text{ODP}(x) = (\text{fractional release factor}) \cdot \alpha \cdot \frac{\tau_x}{\tau_{\text{CFC-11}}} \cdot \frac{M_{\text{CFC-11}}}{M_x} \cdot \frac{n_x}{3} \quad (1-6)$$

where the fractional release factors are discussed in Section 1.4.3 above, α is the relative effectiveness of any halogen compared with chlorine for ozone destruction (taken to be

Table 1-4. Fractional release factors relative to CFC-11 (CCl₃F).

Compound	Relative Fractional Release Factor ^a	Schauffler et al. (2002) ^b	Notes
CFC-11	1		By definition
CFC-12	0.60	0.57 ± 0.05	1
CFC-113	0.75	0.65 ± 0.05	1
CFC-114		0.28 ± 0.02	
CFC-114a		0.63 ± 0.10	
CCl ₄	1.06	1.14 ± 0.06	1
HCFC-22	0.35	0.29 ± 0.02	1
CH ₃ CCl ₃	1.08	1.29 ± 0.16	1
HCFC-123	1.11		1
HCFC-124	0.52		1
HCFC-141b	0.72	0.23 ± 0.11	1
HCFC-142b	0.36	0.08 ± 0.04	1
HCFC-225ca	1.1		2
HCFC-225cb	0.5		2
CH ₃ Cl	0.80	0.85 ± 0.03	2, 3
CH ₃ Br	1.12		4
Halon-1301	0.62		4
Halon-2402	1.22		4
Halon-1211	1.18	1.24 ± 0.07	4

Notes for Relative Fractional Release Factors in column 2:

1. Daniel et al. (1995).
2. WMO (1999).
3. Solomon et al. (1992).
4. Schauffler et al. (1999).

^a These fractional release estimates are used after multiplication by 0.8 (to account for absolute fractional release of CFC-11) in the calculation of EESC (Table 1-17; Section 1.8). See Notes above for references.

^b Estimated for stratospheric air having a mean age of 2-4.5 years.

45 here for bromine; Daniel et al., 1999), τ_x is the global lifetime of the long-lived, well-mixed gas, M_x is the molecular weight, and n_x is the number of halogen atoms.

Daniel et al. (1999) have discussed, specifically for bromine, the definitions and determination of the effectiveness parameter, α , of a halogen radical family in catalyzing ozone destruction, relative to the chlorine radical family. Their suggested definition of α , to be most useful in the ODP definition given in Equation (1-6) above, is cast in terms of the column response of ozone perturbation to inorganic halogen change. Although appearing as a single, fixed, global quantity, it is actually an integrated result with sensitivity to both kinetic parameters for chlorine species and the other halogen of interest, and to atmospheric transport behavior. For this reason, there is no simple way to adjust α quantitatively to reflect new determinations, for example, of individual rate coefficients.

Because a single global value is required by the ODP definition, α represents the global correlation of local photochemical behaviors, for the catalyst of interest (e.g., bromine) and chlorine, with the distribution of ozone

loss. Relative effectiveness for localized regions may differ substantially. For example, Chipperfield and Pyle (1998) model a value of 60 for bromine in the Arctic vortex. The value of 45 used here represents a midlatitude result, which is intended to be more representative of the global mean relative to ozone depletion. An important point made by Danlin et al. (1996) and Chipperfield and Pyle (1998) is that the relative effectiveness, α , can be sensitive to the atmospheric state. Bromine is more effective relative to chlorine in the Arctic vortex for higher inorganic chlorine levels in the range of 2-4 ppb. Semiempirical ODP values calculated for the current atmosphere will be different from values calculated for a future atmosphere containing less chlorine and altered distributions of ozone loss.

Daniel et al. (1999) based their result on DeMore et al. (1997), which did not make a recommendation for products of the OH + chlorine monoxide (ClO) reaction, but discussed studies showing the predominant product channel is hydroperoxyl radical (HO₂) + Cl. Sander et al. (2000) do recommend a value for the product channel

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Table 1-5. Updated Ozone Depletion Potentials for long-lived halocarbons.

Halocarbon	Updated Model-Derived ^a	Updated Semiempirical ^b	Semiempirical Schauffler et al. (2002) ^c	WMO (1999) Model	WMO (1999) Semiempirical	Montreal Protocol
CFC-11		1				
CFC-12		1.0	0.96	0.82	0.9	1.0
CFC-113		1.0	0.90	0.90	0.9	0.8
CFC-114	0.94		1.00	0.85		1.0
CFC-115	0.44			0.40		0.6
Halon-1301		12		12	13	10.0
Halon-1211		6.0	6.0	5.1	5	3.0
Halon-2402		< 8.6				6.0
Halon-1202		1.3 ^d				
CCl ₄		0.73	0.78	1.20		1.1
CH ₃ CCl ₃		0.12	0.15	0.11	0.12	0.1
HCFC-22		0.05	0.041	0.034	0.05	0.055
HCFC-123		0.02		0.012	0.02	0.02
HCFC-124		0.02		0.026		0.022
HCFC-141b		0.12	0.037	0.086	0.1	0.11
HCFC-142b		0.07	0.014	0.043	0.066	0.065
HCFC-225ca		0.02		0.017	0.025	0.025
HCFC-225cb		0.03		0.017	0.03	0.033
CH ₃ Cl		0.02				
CH ₃ Br		0.38		0.37	0.37 ^e	0.6

Upper limits for selected hydrofluorocarbons

HFC-134a	< 1.5 × 10 ⁻⁵
HFC-23	< 4 × 10 ⁻⁴
HFC-125	< 3 × 10 ⁻⁵

^a Calculated from ODPs reported in Table 11-1 of WMO (1999) with lifetimes from Table 1-3 in this chapter.

^b Calculated with updated lifetimes (Table 1-3) and fractional release factors (column 2, Table 1-4) except in the case of Halon-1202.

^c Calculated with updated lifetimes (Table 1-3) and fractional release factors from Schauffler et al. (2002) (column 3, Table 1-4).

^d Derived from the semiempirical estimate in WMO (1991) by considering updated lifetimes for Halon-1202 and CFC-11 (Table 1-3) and an alpha of 45.

^e Value was erroneously reported in Table 11-1 of WMO (1999) as 0.57.

forming HCl, based on Lipson et al. (1999). Including this product channel can substantially diminish the modeled ClO abundance in the mid-stratosphere, by as much as a factor of 2. In reducing the fraction of inorganic chlorine present in the active ClO form, the new recommendation has the effect of moderating the chlorine-induced ozone change in that region, and consequently increasing the modeled efficiency of bromine relative to chlorine. Quantifying the change would require a comprehensive reanalysis, but because the region most affected contributes a relatively small portion of the column ozone change, the overall value for α should not change greatly, and the estimate of 45 from Daniel et al. (1999) remains the best available at the present time.

To separate their study of the effectiveness parameter, α , from the effects of halogen fractional release dis-

tributions for any source gas, Daniel et al. (1999) assumed a hypothetical bromine source species characterized by the CFC-11 fractional release pattern. They point out that sources with significantly shorter atmospheric lifetimes than CFC-11 would also be characterized by greater fractional release lower in the stratosphere, which would produce a larger effectiveness parameter value. The effect for iodine source species would be even more pronounced than for bromine sources. This interaction between the fractional release parameter and the effectiveness parameter introduces uncertainty into the ODP estimates and should be analyzed further for new source species of interest and in the light of projected changes in future stratospheric chlorine loading.

Table 1-5 includes both model and semiempirical ODP values. Semiempirical values are calculated using

updated lifetimes and two separate estimates of fractional release factors (listed in Table 1-4). The values for CFC-12 and CFC-113 are updated from the semiempirical ODPs in Table 11-1 of WMO (1999), which were based on the reference lifetimes of WMO (1995), not WMO (1999). The value of 0.38 for CH₃Br is based on a total lifetime of 0.7 years and is essentially unchanged from the semiempirical value given in Table 2-6 of the previous Assessment (Kurylo and Rodríguez et al., 1999) and the model-derived value reported in Table 11-1 of that Assessment (Madronich and Velders et al., 1999). (Note that the semiempirical value given in Table 11-1 of WMO (1999) was incorrectly recorded.) ODPs derived for HCFC-141b and -142b from the new observation-based fractional release factors are much lower than those derived from earlier model calculations (Schauffler et al., 2002; Solomon et al., 1992). Further work will be required to resolve these discrepancies.

1.4.5 Global Warming Potential

Global Warming Potentials (GWPs) are used to estimate the integrated climate forcing of various greenhouse gases compared with a reference gas, usually chosen to be carbon dioxide (CO₂). They provide a simple way to gauge how decisions affecting greenhouse gas emissions (e.g., in the Kyoto Protocol) may influence our future climate in a relative sense (see, e.g., Ramaswamy et al., 2001, and references therein). Furthermore they allow the effects of these potential actions to be roughly assessed in terms of a “carbon dioxide equivalent” emission. Radiative effects of CFC alternatives are also assessed with the use of GWPs.

Because of the recent publication of *Climate Change 2001: The Scientific Basis* (IPCC, 2001), we only report updates to that work here. We refer the reader to Chapter 6 of IPCC (2001) for a thorough discussion of radiative forcing and GWPs.

The GWP of a particular compound is defined as the ratio of the time-integrated radiative forcing from the instantaneous emission of 1 kg of some gas relative to that of 1 kg of a reference gas. Mathematically, the GWP is given by

$$\text{GWP}_x(\text{TH}) = \frac{\int_0^{\text{TH}} a_x \cdot [x(t)] dt}{\int_0^{\text{TH}} a_r \cdot [r(t)] dt} \quad (1-7)$$

where a_x is the radiative forcing of a unit mass of species x added to the current atmospheric composition, $x(t)$ is the atmospheric decay function of the pulse of species x , a_r

and $r(t)$ are the corresponding quantities for the reference gas, and TH is the time horizon over which the calculation is performed. The response function used in this chapter is the same as in Granier and Shine et al. (1999) and IPCC (2001). The formula for calculating $r(t)$ where CO₂ is the reference gas is also the same as in Granier and Shine et al. (1999) and Ramaswamy et al. (2001). We have adopted a present-day mixing ratio of atmospheric CO₂ of 370 ppm (μmol mol⁻¹; see Section 1.7.1), higher than that of both Granier and Shine et al. (1999) and Ramaswamy et al. (2001) (364 ppm), reflecting the continued increasing atmospheric abundance of this radiatively important gas. This increased CO₂ abundance, relative to Ramaswamy et al. (2001), leads to a decrease in the radiative forcing of a small addition of atmospheric CO₂, and a corresponding increase in all GWPs, of about 1.3%.

1.4.5.1 RADIATIVE FORCING UPDATES

Since Granier and Shine et al. (1999), three comprehensive modeling studies have been published that estimate the radiative forcing efficiency of many radiatively important gases. Two of these, Highwood and Shine (2000) and Jain et al. (2000), were considered in Ramaswamy et al. (2001), and the third, Sihra et al. (2001), was not published until after Ramaswamy et al. (2001). For the majority of gases appearing in Tables 1-6 and 1-7, the radiative forcing efficiencies calculated by Sihra et al. differ from the adopted Ramaswamy et al. (2001) values by less than 20%; for all but one of these gases, we retain the forcing efficiencies adopted for Ramaswamy et al. (2001). HCFC-21 is changed because of an error in its tabulated value in Granier and Shine et al. (1999) and Ramaswamy et al. (2001) (see notes to Table 1-6). Radiative efficiencies for six gases differed by more than 20% between the Sihra et al. (2001) work and Ramaswamy et al. (2001). Revisions to radiative forcing efficiencies for two of these gases (HCFC-123 and HCFC-225ca) are recommended and are discussed in the notes to Table 1-6. For the other four we retain the Ramaswamy et al. (2001) recommendation either because there was no other corroborative calculation to go along with the Sihra et al. (2001) result (i.e., for HFE-143a and H-Galden 1040x) or because the Sihra et al. values differed from those calculated in Jain et al. (2000) by more than 20% (i.e., for CH₃Br and CF₄). The significant differences between Sihra et al. (2001) and Jain et al. (2000) for these and some other gases (e.g., HCFC-225cb, HFC-134a, HFC-227ea, HFC-23, and HFC-32) suggest that further study and understanding is required before adopting new forcing efficiency values for these compounds.

SOURCE GASES

Table 1-6. Direct Global Warming Potentials (mass basis) for gases that have adequately characterized lifetimes.

Industrial Designation or Common Name	Chemical Formula	Radiative Efficiency ($W\ m^{-2}\ ppb^{-1}$)	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
Carbon dioxide	CO ₂	1.53×10^{-5} ^a	^b	1	1	1
Methane	CH ₄	3.7×10^{-4}	12.0 ^c	63 ^d	23 ^d	7 ^d
Nitrous oxide	N ₂ O	3.1×10^{-3}	114 ^c	278	300	158
Chlorofluorocarbons						
CFC-11	CCl ₃ F	0.25	45	6330	4680	1630
CFC-12	CCl ₂ F ₂	0.32	100	10340	10720	5230
CFC-13	CCIF ₃	0.25	640	10160	14190	16520
CFC-113	CCl ₂ FCCIF ₂	0.30	85	6150	6030	2700
CFC-114	CCIF ₂ CCIF ₂	0.31	300	7560	9880	8780
CFC-115	CCIF ₂ CF ₃	0.18	1700	4990	7250	10040
Hydrochlorofluorocarbons						
HCFC-21	CHCl ₂ F	0.14 ^e	1.7	498	148	46
HCFC-22	CHClF ₂	0.20	12.0	4850	1780	552
HCFC-123	CHCl ₂ CF ₃	0.14 ^f	1.3	257	76	24
HCFC-124	CHClFCF ₃	0.22	5.8	1950	599	186
HCFC-141b	CH ₃ CCl ₂ F	0.14	9.3	2120	713	222
HCFC-142b	CH ₃ CCIF ₂	0.20	17.9	5170	2270	709
HCFC-225ca	CHCl ₂ CF ₂ CF ₃	0.20 ^g	1.9	404	120	37
HCFC-225cb	CHClFCF ₂ CCIF ₂	0.32	5.8	1910	586	182
Hydrofluorocarbons						
HFC-23	CHF ₃	0.16	270	9500	12240	10350
HFC-32	CH ₂ F ₂	0.09	4.9	1800	543	169
HFC-41	CH ₃ F	0.02	2.4	304	90	28
HFC-125	CHF ₂ CF ₃	0.23	29	5970	3450	1110
HFC-134	CHF ₂ CHF ₂	0.18	9.6	3200	1090	337
HFC-134a	CH ₂ FCF ₃	0.15	14.0	3370	1320	410
HFC-143	CH ₂ FCHF ₂	0.13	3.5	1160	347	108
HFC-143a	CH ₃ CF ₃	0.13	52	5540	4400	1600
HFC-152	CH ₂ FCH ₂ F	0.09	0.60	176	52	16
HFC-152a	CH ₃ CHF ₂	0.09	1.4	411	122	38
HFC-227ea	CF ₃ CHFCF ₃	0.30	34.2	5760	3660	1200
HFC-236cb	CH ₂ FCF ₂ CF ₃	0.23	13.6	3420	1320	409
HFC-236ea	CHF ₂ CHFCF ₃	0.30	10.7	3850	1350	420
HFC-236fa	CF ₃ CH ₂ CF ₃	0.28	240	7620	9650	7700
HFC-245ca	CH ₂ FCF ₂ CHF ₂	0.23	6.2	2200	682	212
HFC-245fa	CHF ₂ CH ₂ CF ₃	0.28	7.6	3180	1020	316
HFC-365mfc	CH ₃ CF ₂ CH ₂ CF ₃	0.21	8.6	2370	782	243
HFC-43-10mee	CF ₃ CHFCHFCF ₂ CF ₃	0.40	15.9	3890	1610	502
Chlorocarbons						
Methyl chloroform	CH ₃ CCl ₃	0.06	5.0	476	144	45
Carbon tetrachloride	CCl ₄	0.13	26	2540	1380	437
Methyl chloride	CH ₃ Cl	0.01	1.3	56	17	5
Bromocarbons						
Methyl bromide	CH ₃ Br	0.01	0.7	16	5	1

Table 1-6, continued.

Industrial Designation or Common Name	Chemical Formula	Radiative Efficiency ($W\ m^{-2}\ ppb^{-1}$)	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
Bromodifluoromethane	$CHBrF_2$	0.14	5.8	1290	397	123
Halon-1211	$CBrClF_2$	0.30	16	4460	1860	578
Halon-1301	$CBrF_3$	0.32	65	7970	7030	2780
Halon-2402	$CBrF_2CBrF_2$	0.33 ^h	20	3460	1620	505
Fully fluorinated species						
Sulfur hexafluoride	SF_6	0.52	3200	15290	22450	32780
Trifluoromethylsulfurpentafluoride	SF_5CF_3	0.57	800	12370	17500	21500
FC-14	CF_4	0.08	50000	3920	5820	9000
FC-116	C_2F_6	0.26	10000	8110	12010	18280
FC-218	C_3F_8	0.26	2600	5940	8690	12520
FC-31-10	C_4F_{10}	0.33	2600	5950	8710	12550
FC-318	$c-C_4F_8$	0.32	3200	6870	10090	14740
FC-41-12	C_5F_{12}	0.41	4100	6120	9010	13330
FC-51-14	C_6F_{14}	0.49	3200	6230	9140	13350
Halogenated alcohols and ethers						
	$(CF_3)_2CFOCH_3$	0.31	3.4	1130	338	105
	$(CF_3)_2CHOH$	0.28	2.0	718	214	66
HFE-125	CHF_2OCF_3	0.44	136	12970	14670	8530
HFE-134	CHF_2OCHF_2	0.45	26	11470	6220	1970
HFE-143a	CH_3OCF_3	0.27	4.3	2480	744	231
HFCE-235da2	$CHF_2OCHClCF_3$	0.38	2.6	1150	343	107
HFE-245cb2	$CH_3OCF_2CF_3$	0.32	5.1	2300	697	216
HFE-245fa2	$CHF_2OCH_2CF_3$	0.31	4.9	2150	649	201
HFE-254cb2	$CH_3OCF_2CHF_2$	0.28	2.6	1190	353	110
HFE-347mcc3	$CH_3OCF_2CF_2CF_3$	0.34	5.2	1860	566	176
HFE-356pcf3	$CHF_2OCH_2CF_2CHF_2$	0.39	3.6	1660	494	153
HFE-374pcf ⁱ	$CH_3CH_2OCF_2CHF_2$	0.25	5	1810	548	170
HFE-7100	$C_4F_9OCH_3$	0.31	5	1310	397	123
HFE-7200	$C_4F_9OC_2H_5$	0.30	0.77	189	56	17
H-Galden 1040x ^j	$CHF_2OCF_2OC_2F_4OCHF_2$	1.37	6.3	5940	1840	572
HFE-236ca12	$CHF_2OCF_2OCHF_2$	0.66	12.1	7560	2780	864
HFE-338pcc13	$CHF_2OCF_2CF_2OCHF_2$	0.87	6.2	4770	1480	459

Lifetimes are from Table 1-3. GWPs for some gases that were tabulated in IPCC (2001) are not reported here because they have lifetimes less than 0.5 years (see notes to Table 1-3).

^a Assumes a global surface mean mixing ratio of 370 ppm.

^b CO_2 atmospheric response function is as described in WMO (1999) and Ramaswamy et al. (2001).

^c These lifetimes are adjustment times including feedbacks of emissions on lifetimes (see Ramaswamy et al., 2001).

^d The GWPs listed for methane include indirect effects of tropospheric ozone production and stratospheric water vapor production (Solomon and Wuebbles et al., 1995; Ramaswamy et al., 2001).

^e The Sihra et al., (2001) radiative efficiency for HCFC-21 of $0.14\ W\ m^{-2}\ ppb^{-1}$ is adopted rather than the $0.17\ W\ m^{-2}\ ppb^{-1}$ value in WMO (1999) and Ramaswamy et al. (2001). The value of 0.17 was incorrectly tabulated in WMO (1999) (see Sihra et al. (2001) for discussion of error).

^f The radiative efficiency from Sihra et al. (2001) and Jain et al. (2000) was adopted here because these studies were in good agreement and because the estimate adopted by Ramaswamy et al. (2001) originated from Fisher et al. (1990), in which a lower resolution calculation was performed.

^g The radiative efficiency from Sihra et al. (2001) and Jain et al. (2000) was adopted here because these studies were in good agreement and because the estimate adopted by Ramaswamy et al. (2001) was based upon an unpublished calculation made for WMO (1995).

^h Radiative efficiency from Sihra et al. (2001).

ⁱ Referred to as HFE-374pcf2 in past Assessments; however, the current name unambiguously defines the compound.

^j Also known as HFE-43-10pccc124.

SOURCE GASES

Table 1-7. Direct Global Warming Potentials (mass basis) relative to carbon dioxide for gases whose lifetimes are determined only by indirect means rather than by laboratory measurements, or for which uncertainty exists in our understanding of the important loss processes.

Industrial Designation or Common Name	Chemical Formula	Radiative Efficiency ($\text{W m}^{-2} \text{ppb}^{-1}$)	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
Nitrogen trifluoride	NF_3	0.13	740	7780	10970	13240
Perfluorocyclopropane	c- C_3F_6	0.42	>1000	>11950	>17070	>21920
HFE-227ea	$\text{CF}_3\text{CHFOCF}_3$	0.40	11.0	4270	1520	471
HFE-236ea2	$\text{CHF}_2\text{OCHF}_3$	0.44	5.8	3170	973	302
HFE-236fa	$\text{CF}_3\text{CH}_2\text{OCF}_3$	0.34	3.7	1610	480	149
HFE-245fa1	$\text{CHF}_2\text{CH}_2\text{OCF}_3$	0.30	2.2	948	282	88
HFE-329mcc2	$\text{CF}_3\text{CF}_2\text{OCF}_2\text{CHF}_2$	0.49	6.8	2880	904	281
HFE-338mcf2	$\text{CF}_3\text{CF}_2\text{OCH}_2\text{CF}_3$	0.43	4.3	1810	543	169
HFE-347mcf2	$\text{CF}_3\text{CF}_2\text{OCH}_2\text{CHF}_2$	0.41	2.8	1240	368	114
HFE-356mec3	$\text{CH}_3\text{OCF}_2\text{CHF}_3$	0.30	0.94	334	99	31
HFE-356pcc3	$\text{CH}_3\text{OCF}_2\text{CF}_2\text{CHF}_2$	0.33	0.93	363	108	34
HFE-356pcf2	$\text{CHF}_2\text{CH}_2\text{OCF}_2\text{CHF}_2$	0.37	2.0	876	260	81
	$(\text{CF}_3)_2\text{CHOCHF}_2$	0.41	3.1	1250	373	116
	$-(\text{CF}_2)_4\text{CH}(\text{OH})-$	0.30	0.85	239	71	22

All lifetimes were taken from Ramaswamy et al. (2001). The GWPs differ from those in Ramaswamy et al. (2001) because an additional significant figure was retained and because an updated CO_2 mixing ratio was assumed (370 ppm).

1.4.5.2 DIRECT GLOBAL WARMING POTENTIALS

The “direct” portion of a compound’s GWP represents the part that is due to the infrared absorptive and emissive properties that lead to a reduction in the net radiation exiting the troposphere. Here we have divided our compilation of direct GWPs into two tables. Table 1-6 includes compounds whose lifetimes are relatively well established, whereas Table 1-7 has compounds whose lifetimes are more uncertain, either because of a dearth of laboratory measurements or an incomplete understanding of the loss processes. Compounds characterized by lifetimes less than 0.5 years are not included in the tables because of the difficulties involved in making meaningful estimates of a global lifetime and a global radiative effect. In comparing Tables 1-6 and 1-7 with past direct GWP tables (e.g., Granier and Shine et al., 1999; Ramaswamy et al., 2001), note that there is now an additional significant figure tabulated for all GWP values greater than 10. This does not imply that there is any improvement in the accuracy of the GWP values, which is believed to be $\pm 35\%$. The additional significant figure is included to facilitate tracking GWP changes in the future by reducing the impact of rounding.

1.4.5.3 NET GLOBAL WARMING POTENTIALS

As discussed in past Assessments, the impacts of many chlorocarbons and bromocarbons on climate are complicated by their destruction of stratospheric ozone. The destruction of ozone offsets part, and in some cases all, of the direct forcing for the period in the future when ozone destruction occurs. Table 1-8 includes estimates of these net GWPs for selected halocarbons. These values are updated from Daniel et al. (1995) for revised halocarbon lifetimes (Table 1-3), assumption of the relative effectiveness for ozone destruction of bromine compared with chlorine (assumed to be 45 here), future ozone loss scenario (using EESC from scenario Ab; see Section 1.8), and time of emission (assumed in year 2002 here).

The net GWP values here differ from those in Ramaswamy et al. (2001) primarily because of the different assumed time of emission of the radiatively active compound in conjunction with the time dependence of polar and global ozone depletion.

1.4.6 Hydroxyl Radical Changes with Time

Reaction with tropospheric hydroxyl radical (OH) is the chief sink for many of the halocarbons in the com-

Table 1-8. Net Global Warming Potentials of selected halocarbons (on an equal mass basis).

Species	Time Horizon = 2022 (20 years)			Time Horizon = 2102 (100 years)		
	Direct	Net		Direct	Net	
		Min	Max		Min	Max
CFC-11	6330	-938	4910	4680	-524	3660
CFC-12	10340	6660	9620	10720	7660	10120
CFC-113	6150	1770	5290	6030	2470	5330
HCFC-22	4850	4020	4690	1780	1420	1710
HCFC-123	257	-147	177	76	-44	53
HCFC-124	1950	1490	1860	599	450	570
HCFC-141b	2120	-34	1700	713	-109	552
HCFC-142b	5170	4260	4990	2270	1810	2180
CH ₃ CCl ₃	476	-2080	-26	144	-659	-13
CCl ₄	2540	-5460	972	1380	-3440	433
CH ₃ Br	16	-7650	-1490	5	-2270	-444
Halon-1211	4460	-67410	-9630	1860	-33360	-5050
Halon-1301	7970	-77490	-8780	7030	-59280	-5970

Net Global Warming Potentials are calculated from updated lifetimes and radiative data reported in this chapter, and include the indirect cooling effects that result from stratospheric ozone depletion as well as the direct radiative effects. The magnitude of the cooling is estimated using the future EESC of scenario Ab, a value for alpha of 45, and an emission pulse in the year 2002. The min/max ranges of the net GWPs reflect the uncertainty in the change in ozone radiative forcing from 1980 to 1990 of -0.153 to -0.03 W m^{-2} (Ramaswamy et al., 2001).

pendium of ODPs and GWPs discussed in this chapter. The halocarbon lifetimes, on which the ODPs and GWPs depend, are determined by the morphology of the steady-state halocarbon distributions, the kinetics of the OH reaction, and the OH distribution. The time horizon for halocarbon effects summarized by ODPs and GWPs is decades to centuries, and halocarbon lifetimes with respect to tropospheric losses can be decades. It is noteworthy that time invariance of the lifetimes is a typical assumption made to simplify the explanation of these concepts, which also effectively implies an unchanging OH distribution. Karlsdóttir and Isaksen (2000), however, present a multi-dimensional model result for the period 1980-1996 that produces an increase in mean global tropospheric OH levels of 7% over the period, driven largely by increases in low-latitude emissions of nitrogen oxides (NO_x) and carbon monoxide (CO).

The distribution of OH is controlled by local photochemistry comprising the interactions of ozone, water, solar ultraviolet radiation, CO, methane (CH_4), nitrogen oxides, and higher hydrocarbons. Wang and Jacob (1998) describe the relationship of OH abundance to a ratio of nitrogen oxide and hydrocarbon concentrations and ascribe the apparent constancy of OH over the historical industrial period to the conservation of this ratio even as emissions for both increased. The model and analysis of

Wang and Jacob (1998) suggests a 9% decline in weighted global OH from preindustrial time, but Prather and Ehhalt et al. (2001) note that no consensus exists on the magnitude of this change.

The importance of the OH distribution and its changes with time in the context of this chapter includes the effect of interannual variability on the methyl chloroform (CH_3CCl_3) reference OH lifetime. On longer time scales, changes in the OH distribution would change some halocarbon lifetimes, ODPs, and GWPs, increasing or decreasing their impacts relative to the current values. Future increases in direct and indirect greenhouse gases could produce these changes through direct participation in OH-controlling chemistry, indirectly through stratospheric ozone changes that could increase solar ultraviolet in the troposphere, and potentially through climate change effects on biogenic emissions, humidity, and clouds. Prinn et al. (2001) analyzed a 22-year record of global CH_3CCl_3 measurements and emission estimates and suggest that global OH over that period varied from about 5% above to 10% below the period average. This inferred variability in OH contributes to the uncertainty of the reference CH_3CCl_3 lifetime and other lifetimes based on it. These results through 1993 are essentially consistent with the conclusions of Krol et al. (1998, 2001), who used the same measurement and emission record but

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an independent calculation technique to infer an increase of $0.46\% \text{ yr}^{-1}$ over the shorter period of 1978-1993. Prinn et al. (2001) infer that OH values in the late 1990s are below those in the late 1970s to early 1980s, in agreement with the longer CH_3CCl_3 lifetime reported by Montzka et al. (2000) for 1998-1999 relative to the Prinn et al. (2001) value for the full-period average. Inferences regarding methyl chloroform lifetimes or trends in OH are quite sensitive to any errors in the absolute magnitude of estimated emissions. These errors could be significant and enhanced during the late 1990s because annual emissions were dropping precipitously then. Independent estimates of methyl chloroform emissions and their changes during the late 1990s would provide a useful independent assessment of these implied trends in global OH.

IPCC (Prather and Ehhalt et al., 2001), using scenarios generated by the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000) and on the basis of a comparison of results from 14 models, predicts that global OH could vary from a 20% decrease to a 6% increase by 2100. The range of these predicted changes is not materially greater than that already calculated by Prinn et al. (2001). On the other hand, a 9% decrease from preindustrial time to the present and a projected 20% decrease present to future would, in combination, give a substantial change from the preindustrial atmospheric state. The sense of the change is indicated to be most likely in the direction of longer halocarbon lifetimes with respect to oxidation by OH and enhanced atmospheric effects.

1.4.7 Other Sinks

Atmospheric in situ halocarbon sinks include photolysis and homogeneous gas-phase reactions with OH, Cl, and $\text{O}(^1\text{D})$. The dynamics of tropospheric mixing exposes tropospheric air to contact with the surface and allows for irreversible deposition as well. Organisms in surface ocean waters can both consume and produce halocarbons. Chemical degradation of dissolved halocarbons can also occur through hydrolysis. Physical dissolution into ocean waters occurs, but does not represent a significant sink for these halocarbons. These processes are highly variable in the ocean, depending on physical processes of the ocean mixed layer, temperature, productivity, surface saturation, and other variables. Determining a net global sink through observation is a difficult task. Yvon-Lewis and Butler (2002) have constructed a high-resolution model of the ocean surface layer, its interaction with the atmosphere, and physical, chemical, and biological ocean processes. They examined ocean uptake for a range of halocarbons, from knowledge of solubilities and chemical and biological

degradation rates. Although they do not find the ocean sink to be significant for HFCs and HCFCs compared with in situ atmospheric sinks, the reported 94-year oceanic loss lifetimes for CH_3CCl_3 and, coincidentally, for CCl_4 as well, must be included in determining the total lifetimes of these compounds.

Particular consideration of these surface sinks is pertinent for the halocarbons that serve as reference compounds, e.g., CFC-11 and CH_3CCl_3 , and for halocarbons with negligible atmospheric sinks. Kutsuna et al. (2000) have observed degradation of CH_3CCl_3 on the surface of aluminosilica clay mineral surfaces under laboratory conditions. They conclude that both on suspended particles under dust-storm conditions and on surface material in deserts, local sink rates may grow large enough to come within an order of magnitude of atmospheric sinks. Estimates of sink magnitudes on a global basis are not yet available, but would appear to be small.

1.5 METHYL BROMIDE AND METHYL CHLORIDE

Methyl bromide and methyl chloride differ from the other “long-lived” ozone-depleting gases because they have significant natural and anthropogenic sources. Recent research has focused on identifying and quantifying the natural sources and sinks of these two compounds. The calculated atmospheric budgets of both gases are largely out of balance, with identified sinks outweighing identified sources.

1.5.1 Methyl Bromide (CH_3Br)

Since the 1998 Scientific Assessment (WMO, 1999), many publications have appeared and have addressed the atmospheric history of methyl bromide (CH_3Br), its concentration and distribution in the atmosphere (see Section 1.2.1.6 of this chapter), its oceanic and terrestrial fluxes, and its mechanisms of production and degradation in nature. These studies have allowed for refinements in our understanding of atmospheric methyl bromide, but many of the significant uncertainties in 1998 remain. Although new sources have been identified, they do not balance current estimates of loss, which remain essentially unchanged from the previous Assessment (Table 1-9). Analyses of firm air provide for the first time an inferred, 20th century trend for atmospheric methyl bromide in the Southern Hemisphere. These results may provide additional constraints to our understanding of source and sink magnitudes. Interlaboratory differences for absolute calibration of atmospheric methyl bromide are approximately 10%.

Table 1-9. Summary of the estimated source and sink strengths of methyl bromide (CH₃Br).

Source or Sink Type	Source or Sink Best Estimate (Gg yr ⁻¹)	Source or Sink Full Range (Gg yr ⁻¹)
Sources		
Ocean ^a	63	23 to 119
Fumigation–soils ^b	26.5	16 to 48
Fumigation–durables ^b	6.6	4.8 to 8.4
Fumigation–perishables ^b	5.7	5.4 to 6.0
Fumigation–structures ^b	2	2 to 2
Gasoline	5	0 to 10
Biomass burning	20	10 to 40
Wetlands*	4.6	2.3 to 9.2
Salt marshes*	14	7 to 29
Shrublands*	1	0.5 to 2
Rapeseed*	6.6	4.8 to 8.4
Rice fields*	1.5	0.5 to 2.5
Fungus*	1.7	0.5 to 5.2
Peatlands*	0.9	0.1 to 3.3
<i>Subtotal (Sources)</i>	<i>159</i>	<i>77 to 293</i>
Sinks		
Ocean ^a	–77	–37 to –133
OH and hv	–80	–60 to –100
Soils ^c	–47	–32 to –154
Plants	(not quantified)	(not quantified)
<i>Subtotal (Sinks)</i>	<i>–204</i>	<i>–129 to –387</i>
Total (Sources + Sinks)^d	–45	–220 to +71

See text for further explanation and references related to the values listed. Ranges listed for wetlands and shrublands were assumed here to be a factor of 2. Loss due to hydroxyl has been revised, considering the updated analysis of methyl chloroform (see Section 1.4). Table is adapted and augmented from Yvon-Lewis (2000).

* All asterisked items were estimated from measurements of net fluxes and may be influenced by sinks within them. Thus, they represent minimum gross fluxes.

^a The oceanic source has been adjusted to accommodate the slightly smaller undersaturations reported since the 1998 Assessment (WMO, 1999; see text). The source is calculated as source = net oceanic flux – sink, where net oceanic flux is –14 (–11 to –20) Gg yr⁻¹.

^b Fumigation estimates are taken directly from Kurylo and Rodríguez et al. (1999) and are based upon industrial production data for 1992.

^c Revised uptake to soils is included here as discussed in Varner et al. (1999a), Crill (2000), and Yvon-Lewis (2000).

^d The possible range for sources plus sinks here is not a straightforward calculation of highest and lowest values, because the oceanic net flux must hold to within the range of –11 to –20 Gg yr⁻¹. See p. 2.22 in Kurylo and Rodríguez et al. (1999) for a complete explanation. The total range given in this table is a range of extremes, requiring all sinks to be at their highest values while all sources are at their lowest possible values and vice versa. The likelihood of such occurrences is extremely low. Root mean square error on total sinks of –204 Gg yr⁻¹ is estimated from the indicated full ranges as –157 to –327 Gg yr⁻¹; root mean square error of –45 Gg yr⁻¹ on the sum of sources and sinks is estimated at –171 to +14 Gg yr⁻¹.

1.5.1.1 ANTHROPOGENIC AND ANTHROPOGENICALLY INFLUENCED SOURCES

The main anthropogenic sources of CH₃Br include fumigation of soils for planting and of agricultural products for import and export, biomass burning inasmuch as it is influenced by humans, and automobile emissions from burning of leaded gasoline (Table 1-9). Possible alterations of natural emissions associated with changes

in land-use patterns are not included here, nor are there data available to quantify them.

Methyl bromide use as a fumigant in non-Article 5(1) countries (developed countries as defined by the Montreal Protocol) was scheduled to have begun decreasing after 1998. The Montreal Protocol specifies that production of CH₃Br in developed countries be reduced from the 1991 levels by 25% in 1999 and by 50% in 2001. Data reported to the UNEP Ozone Secretariat

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(UNEP, 2002) are consistent with such a reduction and suggest further that global consumption in 1999 was ~11 Gg less than that in 1998.

Little has changed in our understanding of the degree to which the combustion of leaded fuel contributes to emissions of atmospheric CH₃Br. Currently about 86% of all gasoline sold in the world is unleaded, and this will likely rise to 89% by 2005 (personal communication, M.P. Walsh, international consultant, Arlington, Virginia, U.S., 2001). Automobile emissions today remain a small part of the global budget (5 ± 5 Gg yr⁻¹, or ~3% of the total emissive flux estimated from sinks), although they were substantially larger in the past (Thomas et al., 1997). Similarly, little new information on the emission of methyl bromide from biomass burning has emerged since 1998. The studies of N.J. Blake et al. (1996) and Mano and Andreae (1994) reported in the 1998 Assessment (WMO, 1999) remain our best estimates, supporting globally averaged emissions of 20 (10-40) Gg yr⁻¹.

1.5.1.2 SURFACE INTERACTIONS: NATURAL SOURCES AND SINKS

Ocean

New work continues to confirm that the ocean remains the largest identified source and second largest sink for atmospheric CH₃Br. This has allowed for refinements in our understanding of methyl bromide saturation, and there is some suggestion that methyl bromide in temperate waters is supersaturated in the spring and summer and undersaturated in the fall and winter (King et al., 2000), which is consistent with observations of seasonal cycles in the North Sea by Baker et al. (1999). This could explain some of the apparently anomalous supersaturations in the open ocean observed in previous investigations (e.g., Lobert et al., 1996; Groszko and Moore, 1998), although not all observed saturation anomalies fit such a pattern (e.g., King et al., 2000; Northeastern Atlantic data in Baker et al., 1999). Combining results from the various expeditions, and using a bimodal relationship to temperature similar to that suggested by Groszko and Moore (1998), King et al. (2000) determined that the overall effect of including these seasonal differences on a global scale lowered the estimated net flux slightly downward from -21 (-32 to -3) to -14 (-20 to -11) Gg yr⁻¹. These findings do not affect the estimate of lifetime relative to oceanic loss, but they do reduce the budget imbalance slightly (lifetime relative to oceanic loss is calculated directly from rates of hydrolysis and nucleophilic substitution in seawater and rates of air-sea exchange).

Two isotopic studies of CH₃Br consumption in the open ocean have been published, supporting the earlier

finding of significant biological removal of CH₃Br in seawater (Tokarczyk and Saltzman, 2001; Tokarczyk et al., 2001). The best estimate of the partial lifetime of atmospheric CH₃Br with respect to oceanic loss remains 1.9 (1.1-3.9) years (Yvon-Lewis and Butler, 1997), as reported in the 1998 Assessment (WMO, 1999).

Soils

Soil fluxes of CH₃Br are slightly better constrained than in 1998. The soil sink reported in the 1998 Assessment (WMO, 1999) was large, -42 Gg yr⁻¹, but also included large uncertainties (-214 to -10 Gg yr⁻¹). This wide range stems from two studies reporting substantially different means. Shorter et al. (1995) had estimated a global sink of -42 ± 32 Gg yr⁻¹, whereas Serca et al. (1998) arrived at -143 ± 70 Gg yr⁻¹. The difference between these two studies was in part due to the measurements for cultivated soils, but was also a function of the choice of procedure for extrapolating. The estimate for losses to agricultural soils is much larger in the Serca et al. (1998) study. Because of this, Serca et al. (1998) also suggested a mean flux of -94 ± 54 Gg yr⁻¹ by taking an arithmetic mean of the results from the two studies for agricultural soils. After making additional measurements at 40 globally distributed sites, Varner et al. (1999a) revised their estimate of agricultural losses upward, but only by a small amount. Based upon these new data and considerations of previously reported data, Crill (2000) revised the range for loss of atmospheric methyl bromide to soils, narrowing it to -154 to -32 Gg yr⁻¹. Adjusting the total soil loss for the new measurements of losses to cultivated soils, Yvon-Lewis (2000) suggested a mean flux of -47 Gg yr⁻¹, within the range reported by Crill (2000).

Recent reports have suggested that at least some soils can produce CH₃Br and even emit CH₃Br to the atmosphere. Keppler et al. (2000) identified an abiotic mechanism for the production of halogenated hydrocarbons in soil that yields high production rates. This mechanism involves iron, halide ion, and organic matter, and the reaction can be fast. How much of this production reaches the atmosphere, and whether such production is limited to peatlands or is ubiquitous, is presently unknown. The study of Rhew et al. (2001) showed that shrublands could be a net source or sink of CH₃Br and CH₃Cl. Because this study focused on net fluxes, it does not relate directly to estimates of lifetime.

Plants and Plant Ecosystems

In the 1998 Assessment (WMO, 1999), a potentially significant plant sink was reported but not quantified globally (Jeffers and Wolfe, 1997). Because of a lack

of additional studies related to this loss, calculating a partial lifetime of atmospheric methyl bromide from plants is not yet possible.

In the past 4 years, however, considerable attention has been given to the study of net fluxes from isolated, terrestrial ecosystems. Dimmer et al. (2001) measured CH_3Br net fluxes from Irish peatlands, Varner et al. (1999b) measured net fluxes from New Hampshire wetlands, and Rhew et al. (2000, 2001) studied the net fluxes of methyl bromide from salt marshes and shrublands. Extrapolating these measurements globally yields net flux estimates of 0.9 Gg yr^{-1} for peatlands, 4.6 Gg yr^{-1} for wetlands, and 14 Gg yr^{-1} for salt marshes. Shrublands were reported as having a net flux of $<1 \text{ Gg yr}^{-1}$. Lee-Taylor and Holland (2000), modeled published fungal production rates, deriving a global net flux of 1.7 Gg yr^{-1} . From studying cultivated crops, Gan et al. (1998) calculated a net flux of 6.6 Gg yr^{-1} for rapeseed, and Redeker et al. (2000) calculated a net flux of 1.5 Gg yr^{-1} for rice fields. What is important to note is that all these studies report measurements of net fluxes and, although useful in narrowing the gap between sources and sinks in the atmospheric budget of CH_3Br , they are not suited alone for determining gross fluxes or partial atmospheric lifetimes.

1.5.1.3 ATMOSPHERIC LIFETIME

Although new publications have confirmed biological losses in the ocean, refined the magnitude of losses to soils, and revised our understanding of global OH burdens (see Section 1.4.2), the best estimate of the methyl bromide global lifetime remains 0.7 years (0.5-0.9 year root mean square (rms) uncertainty; 0.4-1.1 year full range; Kurylo and Rodríguez et al. (1999)). A couple of things have the potential to change the calculated atmospheric lifetime of CH_3Br , however. First, the magnitude of the soil sink remains highly uncertain. Measurements have been made that help in reducing uncertainties, but the result also depends upon the method of extrapolation chosen. Furthermore, the determination that any additional sinks, such as plants, might be significant would reduce further the estimated lifetime for methyl bromide.

1.5.1.4 A TWENTIETH CENTURY, SOUTHERN HEMISPHERIC TREND AND ITS IMPLICATIONS

Since the previous Assessment (WMO, 1999), two papers have inferred atmospheric histories for methyl bromide from measurements of Antarctic firn air (Butler et al., 1999; Sturges et al., 2001a). These studies, based upon samples collected at a total of four locations in Antarctica, suggest that mixing ratios of methyl bromide in the Southern Hemisphere have increased by about 3 ppt since

1900 (Figure 1-11). The 2-ppt increase suggested for the latter half of the last century is roughly coincident with the onset of methyl bromide use as a fumigant in the early 1960s (Singh and Kanakidou, 1993), but other sources or sinks also may have changed over that time as well. The rate of increase of about $0.6\% \text{ yr}^{-1}$ from about 1970 to 1990 inferred from firn air agrees with the real-time measurements of Khalil et al. (1993) for the Southern Hemisphere during 1978-1993 and with the data obtained from archived flask air filled at Cape Grim, Tasmania, over this same period (Figure 1-11; Miller, 1998). The

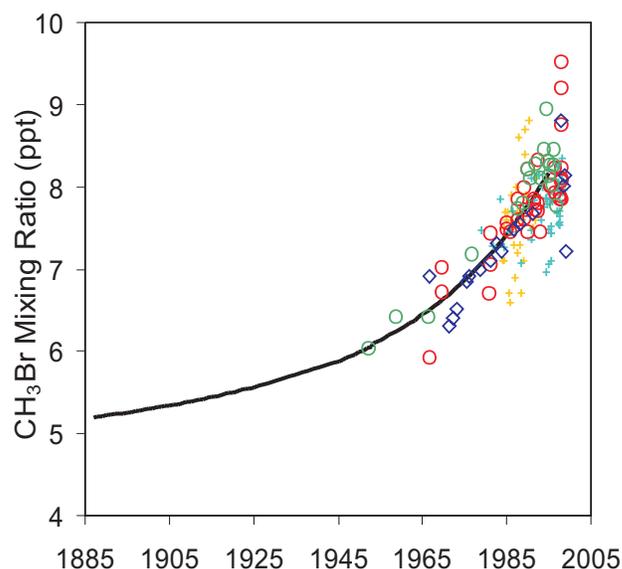


Figure 1-11. Southern Hemispheric history of methyl bromide suggested by Antarctic firn air measurements from four locations, and by archived air samples and flask samples collected at Cape Grim, Tasmania (41°S). The solid line is an atmospheric history derived from firn air measurements at South Pole, Antarctica, estimated with a vertical diffusion model that fits the history of the $\text{CH}_3\text{Br}/\text{CO}_2$ ratio to the observed CO_2 and CH_3Br firn air profiles (see Butler et al., 1999, for details). The green circles are firn data from Siple Dome, Antarctica, plotted against dates determined from CO_2 measurements and the ratio of CH_3Br and CO_2 diffusivities (Butler et al., 1999); the red circles are from firn air at Dronning Maud Land, Antarctica, and are plotted against dates adjusted from CFC-12 measurements and the ratio of CH_3Br and CFC-12 diffusivities (Sturges et al., 2001a); blue diamonds are similar data for Dome C, Antarctica (Sturges et al., 2001a); and yellow (Khalil et al., 1993) and light blue (Miller, 1998) plus symbols are from analyses of flask samples collected at Cape Grim.

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work of Butler et al. (1999), which reported results for firn air dating back to the end of the 19th century, indicated that atmospheric methyl bromide may have increased as much as 1 ppt in the first half of the 20th century, but the causes for this earlier apparent increase, and whether they continued into the latter half of the century, are unknown.

Atmospheric histories derived from the analysis of firn air, however, have significant uncertainties. Dating of firn air is imprecise (Schwander et al., 1988), and the atmospheric histories derived for methyl bromide presume that in situ production or degradation are insignificant during the long time that the firn air is exposed to the surrounding snow. Whereas all Antarctic sites sampled have yielded a similar atmospheric history for CH₃Br regardless of their differences in temperature, deposition rate, depth, and lock-in zone thickness (Figure 1-11), Arctic sites exhibited large elevations of methyl bromide and other gases near the bottoms of the profiles (not shown; Butler et al., 1999; Sturges et al., 2001a). Further, the profiles from the Northern Hemispheric sites differed dramatically from one another, as would be expected for site-specific disturbances. That this was not observed in the Antarctic increases confidence in the reported atmospheric history from these sites. The mechanism for increases of certain compounds, including methyl bromide, at the bottom of the Arctic profiles is not known.

An understanding of atmospheric changes for methyl bromide during the 20th century can provide some insight into the relative magnitude of present-day sources. Of particular interest is the magnitude of industrially derived emissions relative to the total annual flux of methyl bromide. This quantity can be estimated directly from our understanding of source and sink magnitudes: for emissions derived from fumigation of 41 Gg yr⁻¹, with an rms range of 30-62 Gg yr⁻¹, divided by the best estimates for sinks (204 Gg yr⁻¹ and rms range of 157-327; Table 1-9), the calculated contribution of industrially produced methyl bromide to a 10-ppt global atmospheric burden ranges from 10 to 40%. As suggested above, the atmospheric trend inferred from the Antarctic firn air provides a second approach for estimating this fraction. The results suggest that from 1950 to 1995, CH₃Br in the Southern Hemisphere increased by 2 to 2.5 ppt (Figure 1-11). If we assume that either Northern Hemispheric mixing ratios increased by the same proportion as in the Southern Hemisphere or that Northern Hemispheric mixing ratios in 1950 were the same as those in the Southern Hemisphere, then the firn results suggest that CH₃Br in the global atmosphere has increased 25-40% from 1950 to 1995, regardless of lifetime or other budget

considerations. Therefore, were this increase solely due to fumigation, 40% would represent an upper limit for the contribution from fumigation. However, it also appears from the firn data that CH₃Br in the Southern Hemisphere increased about 0.7 ppt during the first half of the century, perhaps because of changing land-use practices, increases in biomass burning, or the post-1925 onset of leaded-fuel combustion in automobiles. If this underlying trend had continued through the second half of the century, then the contribution of industrially produced methyl bromide would be 1.5-3 ppt, or 15-30% of the 1995 atmospheric burden. Given the assumptions above, then, the overall range of 15-40% for this fraction suggests emissions related to fumigation of 30-80 Gg yr⁻¹ in 1995. Although bromine emissions from combustion of leaded fuel have decreased dramatically since 1970, they were similar in 1950 to what they were in 1990 (Thomas et al., 1997) and do not strongly influence this conclusion.

1.5.1.5 ATMOSPHERIC BUDGET

The calculated budget for atmospheric methyl bromide remains out of balance, with estimated sinks still outweighing estimated sources (Table 1-9). However, the new findings on ecosystem net fluxes have narrowed the gap between calculated sources and sinks (Crill, 2000; Yvon-Lewis, 2000; Butler, 2000). The most complete summary is that of Yvon-Lewis (2000), from which Table 1-9 has been adapted and augmented. This budget is for the mid-1990s, before the scheduled reductions of methyl bromide production. Because measurements relating to plants usually involve estimates of net fluxes, any plant sink is incorporated implicitly into the source terms for those elements that are reported as such in the table. Quantifying the plant sink, while affecting the calculated lifetime, would not affect the budget balance.

1.5.2 Methyl Chloride (CH₃Cl)

Methyl chloride (CH₃Cl), the most abundant halocarbon in the atmosphere, is derived largely from natural sources. Until 1996 most of the input to the atmosphere was considered to originate from the oceans, but investigations in recent years have indicated that terrestrial sources, probably located in the tropics, dominate the atmospheric budget, and that these sources are more significant than hitherto appreciated. Moreover, the presumption that abiotic reactions constitute the only sinks for atmospheric CH₃Cl is being displaced by recognition that microbial degradation in soil may represent a measurable sink of atmospheric CH₃Cl. Although new findings have allowed constraints to be placed on some source

terms in the atmospheric budget, major uncertainties still exist regarding the magnitude of several sources and sinks. As is seen for methyl bromide, a shortfall is apparent between known sources and modeled sinks of methyl chloride.

1.5.2.1 ATMOSPHERIC DISTRIBUTION AND TRENDS

There is emerging evidence that CH_3Cl is elevated in air masses associated with land in the tropics (Khalil and Rasmussen, 1999; Yokouchi et al., 2000b; see also Section 1.2.1.7). CH_3Cl mixing ratios of up to 1400 ppt have been recorded in calm weather off the subtropical Okinawa and Hateruma Islands in southern Japan (Li et al., 1999; Yokouchi et al., 2000b) and up to 850 ppt at inland locations on various continents (Khalil and Rasmussen, 1999). Interestingly, the high CH_3Cl mixing ratios observed by the Japanese researchers were strongly correlated with elevated amounts of the plant-derived terpene, α -pinene, which has an atmospheric lifetime of only a few hours. This finding is consistent with high emissions of CH_3Cl from tropical coastlands. In subsequent work on the marine boundary layer in the Western Pacific and Southeastern Indian Ocean, Li et al. (2001) found that the CH_3Cl mixing ratio was enhanced (up to 950 ppt) in air masses derived from forested tropical islands.

An indication of long-term trends in atmospheric CH_3Cl has been obtained by analysis of air trapped in polar firn in Antarctica and Greenland (Figure 1-12; Butler et al., 1999). An increase of about 10% was inferred since the mid-1900s for both hemispheres, suggesting that the anthropogenic contribution, if reflected by the apparent 20th century increase, is comparatively small. Global measurements from 1981-1997 suggest an overall decrease of about 4% over this shorter period (Khalil and Rasmussen, 1999).

1.5.2.2 SOURCES OF ATMOSPHERIC METHYL CHLORIDE

The principal sources of atmospheric CH_3Cl identified to date are biomass burning and the oceans, although tropical plants may exceed all other sources (Yokouchi et al., 2002; Table 1-10). Except for the tropical plant source, the latest estimates of emissions do not differ substantially from those reported in the 1998 Assessment (WMO, 1999; Graedel and Keene, 1999). The net flux from the oceans was revised sharply downward in 1996 to 200-400 Gg yr^{-1} (Moore et al., 1996). This estimate represents the balance between emissions of CH_3Cl in tropical waters and uptake in the cold waters of latitudes above 50°. Khalil et al. (1999) analyzed data collected by several groups of

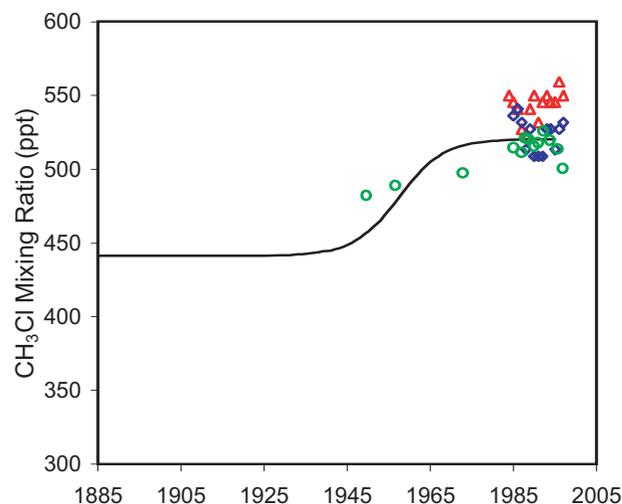


Figure 1-12. Southern Hemispheric history of methyl chloride suggested by Antarctic firn air measurements from two locations, and by atmospheric measurements from flask samples collected in Antarctica and at Cape Grim, Tasmania. The solid line is an atmospheric history derived from firn air measurements at South Pole, Antarctica, estimated with a vertical diffusion model that fits the history of the $\text{CH}_3\text{Cl}/\text{CO}_2$ ratio to the observed CO_2 and CH_3Cl firn air profiles (see Butler et al., 1999, for details). The open green circles are data from Siple Dome, Antarctica, plotted against dates derived from adjusted CO_2 measurements and diffusivities (Butler et al., 1999), and the open blue diamonds and red triangles are annual means of “real-time” measurements from flask samples collected in Antarctica and Cape Grim, respectively (Khalil and Rasmussen, 1999; these data have been lowered by 8.3% to account for a calibration difference).

investigators between 1983 and 1996 and confirmed the weaker oceanic source, calculating a net global flux of 600 Gg yr^{-1} (after adjusting for calibration). For biomass burning, Lobert et al. (1999) estimated emissions of CH_3Cl from nine different burning categories on a 1° latitude by 1° longitude grid. Fluxes were derived from biomass inventories based upon emission ratios relative to both CO and CO_2 and the chlorine content of the fuel feedstock. Calculated global emissions of 911 Gg yr^{-1} (range 655-1125 Gg yr^{-1}) from burning, most of which are believed confined to the tropics and subtropics, agree with the previous approximation of $1.0 \pm 0.5 \text{ Tg yr}^{-1}$ (Andreae et al., 1996; N.J. Blake et al., 1996; Rudolph et al., 1995).

Recently, Yokouchi et al. (2002) suggested that methyl chloride emissions from tropical plants might be

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Table 1-10. Estimated source and sink strengths for atmospheric methyl chloride (CH₃Cl).

Source or Sink Type	Source or Sink Best Estimate (Gg yr ⁻¹)	Source or Sink Full Range (Gg yr ⁻¹)
Sources		
Oceans	600 ^a	325 to 1300
Biomass burning	911 ^b	655 to 1125
Tropical plants	910 ^c	820 to 8200
Fungi	160 ^d	43 to 470
Salt marshes	170 ^e	65 to 440
Wetlands	40 ^{f, g}	6 to 270
Coal combustion	105 ^h	5 to 205
Incineration	45 ^h	15 to 75
Industrial	10 ^h	
Rice	5 ⁱ	
<i>Subtotal (Sources)</i>	<i>2956</i>	<i>1934 to 12,085</i>
Sinks		
Reaction with OH in troposphere	-3180 ^j	-2380 to -3970
Loss to stratosphere	-200 ^a	-100 to -300
Reaction with Cl in marine boundary layer	-370 ^{i, j}	-180 to -550
Microbial degradation in soil	-180 ^k	-100 to -1600
Loss to polar oceans	-75 ^{j, l, m}	-37 to -113
<i>Subtotal (Sinks)</i>	<i>-4005</i>	<i>-2797 to -6533</i>
Total (Sources + Sinks)	-1049	-4599 to +9288

The destructive flux from reaction with OH is calculated with revised OH (see Section 1.4).

^a Khalil et al. (1999), adjusted for calibration.

^b Lobert et al. (1999).

^c Yokouchi et al. (2002).

^d Watling and Harper (1998).

^e Rhew et al. (2000).

^f Varner et al. (1999a).

^g Dimmer et al. (2001).

^h McCulloch et al. (1999); Keene et al. (1999).

ⁱ Redeker et al. (2000).

^j Khalil and Rasmussen (1999), after calibration adjustment applied; see text.

^k Khalil and Rasmussen (2000), after calibration adjustment applied; see text.

^l Moore et al. (1996).

^m Unlike in Table 1-9, loss to polar oceans here is from field observations alone and is given as a net sink.

the largest known source. They determined that a specific group of ferns and trees in Southeast Asia alone produced 910 Gg yr⁻¹, about one-fourth of the annual flux as estimated by sinks. The uncertainty in this estimate is large, and this source certainly warrants additional investigation.

Release of CH₃Cl by wood-rotting fungi has been estimated by Watling and Harper (1998) at 160 Gg yr⁻¹ (Table 1-10), of which 75% is derived from tropical and subtropical forests. This assessment was based on the conservative assumption that only Cl⁻ from wood itself

was available for fungal uptake. If, however, Cl⁻ in leaf litter and soil is accessible to these fungi, emissions could be much greater. Dimmer et al. (2001) reported field measurements of CH₃Cl fluxes from forest floors. Although the sites (conifer plantations in Western Ireland) cannot be regarded as globally representative of temperate coniferous forest, an extrapolation of the observed emission fluxes led to an estimate of 85 Gg yr⁻¹ from such forests worldwide, suggesting that the order of magnitude of the overall flux from fungi in forest ecosystems is similar to that predicted by Watling and Harper (1998).

In addition to the methyl chloride source reported by Yokouchi et al. (2002), Rhew et al. (2000) found large net CH_3Cl fluxes from halophytic plant species in the middle and upper vegetation zones of Californian salt marshes. Assuming that the sites were representative of salt marshes globally, the authors postulated a global flux of 170 Gg yr^{-1} from this source (Table 1-10). Subsequent investigations on shrubland ecosystems in Southern California demonstrated significant emissions from some plant species at particular seasons (Rhew et al., 2001). However, such emissions were counterbalanced by soil uptake during other seasons, and therefore the biome was in fact a small net sink for CH_3Cl . Fluxes of CH_3Cl from peatland ecosystems have been monitored by investigators in Northeastern United States (Varner et al., 1999b) and Western Ireland (Dimmer et al., 2001), although in neither case was it clear whether emissions came from plants or the soil. On the basis of these measurements Varner et al. (1999b) postulated global emissions from wetlands of 48 Gg yr^{-1} , whereas Dimmer et al. (2001) estimated global emissions of 5 Gg yr^{-1} from peatlands and 35 Gg yr^{-1} from wetlands. These estimates must be treated with caution because data in each investigation were restricted to ecologically similar temperate sites and were collected over a short period. Emissions of CH_3Cl have also been noted from the soil of California rice paddies, which have been extrapolated to global emissions of 5 Gg yr^{-1} from this crop (Redeker et al., 2000).

A novel abiotic mechanism for formation of CH_3Cl in soils rich in organic matter in the presence of Fe^{3+} and high chloride concentrations has recently been proposed (Keppler et al., 2000). Such a process may yield significant fluxes in highly saline environments, but no field measurements have yet been conducted. Anthropogenic release of CH_3Cl during coal combustion, incineration, and industrial processes was quantified in the Reactive Chlorine Emissions Inventory (McCulloch et al., 1999). Emissions from these sources contribute in all about 160 Gg yr^{-1} , or less than 10% of total known sources (Table 1-10).

1.5.2.3 SINKS OF ATMOSPHERIC METHYL CHLORIDE

Reaction with OH radical is the dominant pathway for removal of CH_3Cl from the atmosphere. Khalil and Rasmussen (1999) estimated that the atmospheric lifetime of CH_3Cl with respect to OH attack varied from 0.8 years in the tropics to 12 years at the poles, with an average global lifetime of 1.4 years. This partial lifetime has been revised to 1.5 years in this Assessment based upon the considerations discussed in Section 1.4.2. Reaction with chlorine radicals in the marine boundary layer also could constitute another loss process, particularly in tropical lat-

itudes (Keene et al., 1996). Using a chlorine concentration of 5×10^{-4} radicals cm^{-3} in the marine boundary layer, Khalil and Rasmussen (1999) estimated this sink as up to 0.4 Tg yr^{-1} . This would represent a partial atmospheric lifetime of 13 years with respect to this loss alone.

Some evidence exists for a potentially substantial sink of atmospheric CH_3Cl involving microbially mediated uptake by soil (Khalil and Rasmussen, 2000). On the basis of measurements of CH_3Cl uptake by soils from Brazil and Greenland, these authors estimated a global uptake of 0.18 Tg yr^{-1} (0.2 Tg before adjusting for calibration discrepancies) by soils. This number is uncertain, and may be an underestimate; the ubiquitous occurrence in soil from pristine environments of microbial species capable of utilizing CH_3Cl as sole carbon and energy source implies a large and substantial soil sink for CH_3Cl (Harper, 2000; McAnulla et al., 2001). The loss of 0.2 Tg yr^{-1} (0.18 Tg yr^{-1} adjusted for calibration) translates to a partial atmospheric lifetime of 28 years.

Moore et al. (1996) noted undersaturations of CH_3Cl in the polar oceans, which Khalil and Rasmussen (1999) combined with other data to calculate a global, polar sink of 83 Gg yr^{-1} (75 Gg yr^{-1} adjusted for calibration). Uncertainties in the sink term given by Moore et al. (1996) suggest that this value could range from 37 to 113 Gg yr^{-1} . This small sink, if irreversible, amounts to an atmospheric lifetime of ~ 70 years.

Combining the lifetimes of 1.5, 13, 28, and 70 years for losses to reaction with OH, reaction with Cl, consumption in soils, and degradation in seawater, respectively, yields an atmospheric lifetime of 1.3 years for CH_3Cl (Table 1-3).

1.5.2.4 ATMOSPHERIC BUDGET

The imbalance between calculated emissions from known sources and the estimated global sink for atmospheric CH_3Cl is about 1.0 Tg yr^{-1} out of a total estimated flux of 4.0 Tg yr^{-1} (or 25%). All sources quantified to date are situated predominantly in the tropics, a location consistent with source deconvolution calculations. Using a global 3-D model of atmospheric CH_3Cl , Lee-Taylor et al. (2001) were able to reproduce the observations of Khalil and Rasmussen (1999) by adding a tropical terrestrial source of 2.5 Tg yr^{-1} and reducing emissions from Southeast Asia. Any major as-yet-unidentified source must necessarily show a similar global distribution to be consistent with observations. In this context observations of high CH_3Cl mixing ratios in air masses associated with forested tropical coastlines (Yokouchi et al., 2002) are highly significant and should provide a focus for future investigations on potential sources of atmospheric CH_3Cl .

SOURCE GASES

1.6 ATMOSPHERIC HALOCARBON OBSERVATIONS COMPARED WITH EXPECTATIONS

1.6.1 Consistency Between Atmospheric Halocarbon Measurements and Known Sources and Sinks

Consistency between atmospheric measurements and known sources and sinks for halocarbons are assessed here in two complementary ways: (1) atmospheric measurements are compared with mole fractions that are calculated from emissions derived from industrial production data (see Section 1.3), and (2) the industry-based annual emission estimates are compared with global emissions inferred from the atmospheric measurements. The measurements we consider here are global means estimated from multiple surface sampling sites (the AGAGE, CMDL, and UCI monitoring networks; D.R. Blake et al., 1996; Montzka et al., 1999; Prinn et al., 2000) and global means inferred from measurements at a single site (the Australian air archive, Langenfelds et al., 1996; Fraser et al., 1996). Calculations were performed with two-dimensional models (Cunnold et al., 1994, 1997; Fraser et al., 1999; Oram et al., 1995). Any unexpected differences between the calculated and observed mixing ratios or the calculated and the industry-based emission estimates may represent unaccounted for production and emissions, but these differences may also arise from systematic errors in measurement calibration or consistency, in halocarbon loss rates (lifetimes), or in modeling the atmosphere.

1.6.1.1 CFCs

Measured mixing ratios for CFC-11 and -12 are 5-10% higher than those calculated from emissions derived from production data throughout the entire period of measurement (Figure 1-13). For CFC-12 during the 1990s the discrepancy became small compared with the uncertainties in this analysis. For both these gases, mixing ratios reported by different laboratories agree quite well (Table 1-1), and this consistency argues against measurement error being the source of the discrepancies.

The differences noted for mixing ratios are also apparent in a comparison of emissions derived from measurements or industry production data before 1992 (Figure 1-14). The observations before that year suggest approximately 5-10% larger emissions of CFC-11 and -12 compared with those derived from industry production data. After 1992 the uncertainties in the analysis become large, and any discrepancies are well within this uncertainty. In the case of CFC-11, these differences also could be reconciled if its lifetime were somewhat longer than the cur-

rent best estimate of 45 years (see Section 1.4). For CFC-12, scaling the lifetime by some constant factor cannot remove these differences; in fact it seems most likely that the industry emissions estimates from 1993 to 1997 are slightly high. This is consistent with improved containment of CFCs in applications (UNEP, 1998a), although the extent to which practices to reduce ODSs emissions have been adopted is difficult to ascertain.

Past discussion regarding CFC-113 noted that observations substantially underestimated calculated global means (Fraser et al., 1996; Prinn and Zander et al., 1999; Figure 1-13). This situation stems from the presumption in these studies that significant amounts of CFC-113 were produced by companies not reporting to AFEAS. However, it is now apparent that the only significant source that is not counted by AFEAS is Russian production (Bingfeng et al., 2000). The actual Russian production is unknown, but capacity for CFC-113 amounted to some 12,000 tons yr⁻¹ prior to the total shutdown that was accomplished there in 2000 (personal communication, E. Pedersen, World Bank, 2002). This represents a maximum of 5% of the 1989 reported production, with resulting emissions significantly less than the confidence limits on global emissions (Figure 1-14). The global emissions inferred from measurements are generally consistent with AFEAS data accounting for global production of this gas. There is a small divergence after 1995 for reasons not currently understood (Figure 1-14).

1.6.1.2 METHYL CHLOROFORM

For methyl chloroform artificially good agreement is shown in Figure 1-13, because industry release estimates are used here to derive the OH field and methyl chloroform lifetime (Prinn et al., 2001). An independently calculated OH field by Spivakovsky et al. (2000) results in a methyl chloroform lifetime within 10% of that inferred by Prinn et al. (2001), but a number of other models of the OH distribution give much larger differences (e.g., Hein et al., 1997; Hauglustaine et al., 1998). The small discrepancy between the measured and expected mixing ratios after 1996 has been interpreted as indicating lower OH values at that time (Prinn et al., 2001). On the basis of an uncertainty of approximately 3% (except during 1996-1999) for industry-based emissions of methyl chloroform, it has been concluded that the effective OH in a 12-box, 2-D model averaged from 1979 to 2000 has an uncertainty of $\pm 14\%$ (Prinn et al., 2001).

1.6.1.3 CARBON TETRACHLORIDE

With loss to the ocean now included (Yvon-Lewis and Butler, 2002), the lifetime of carbon tetrachloride is

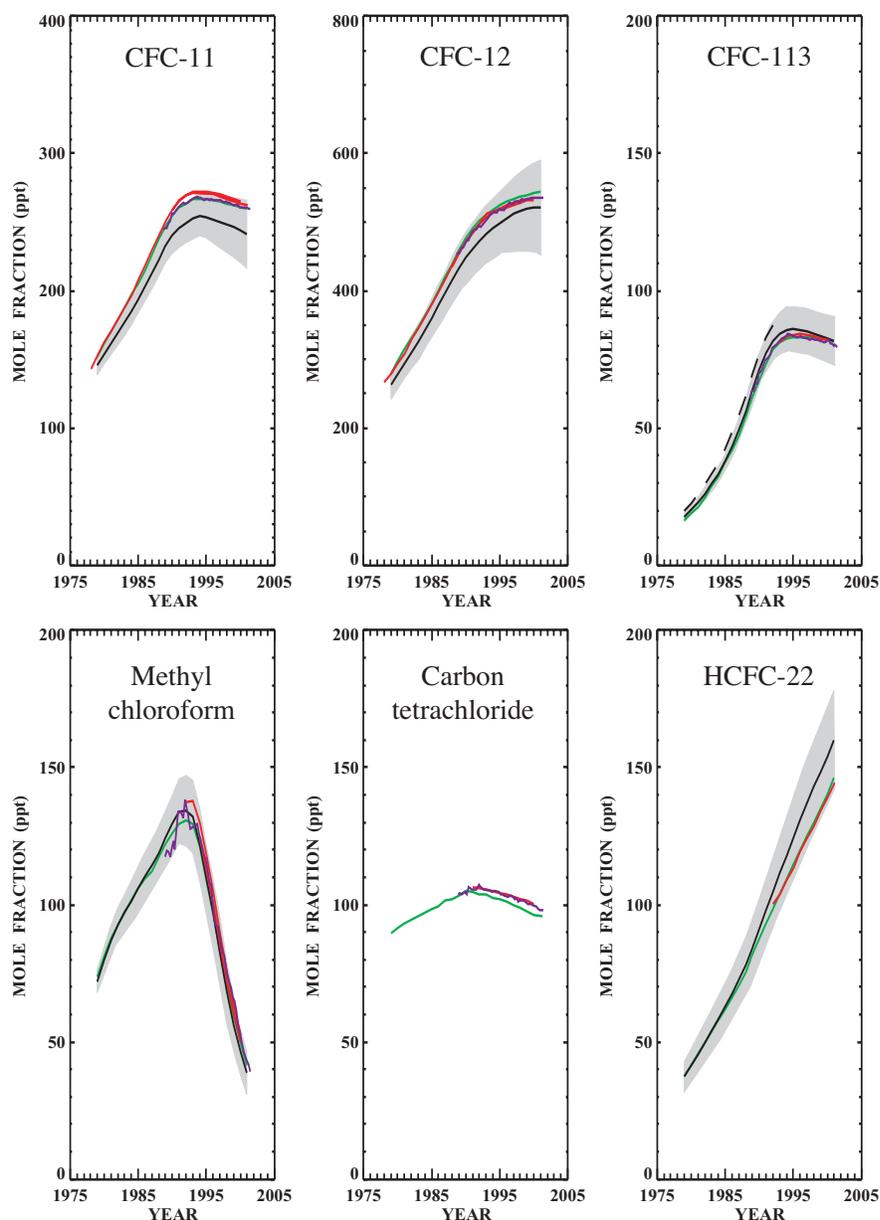


Figure 1-13. Measured and calculated global mean surface mixing ratios for major CFCs, methyl chloroform, carbon tetrachloride, and HCFC-22. Observations are from AGAGE in situ instruments (green lines: Prinn et al., 2000), from CMDL in situ instruments and flask measurements (red lines: Montzka et al., 1999), and from UCI flask measurements (purple lines: D.R. Blake et al., 1996, all gases except HCFC-22). For HCFC-22, the AGAGE global means before 1992 are derived from measurements of the Australian air archive (Miller et al., 1998) and a 12-box model calculation. Global surface mixing ratios were calculated with a 12-box model (Cunnold et al., 1997) using global emissions from a combination of AFEAS (2001) and UNEP (2002) data and lifetimes of 45 (29-76), 100 (77-185), 85 (54-143), 5.0 (4.5-5.6), and 12.0 (10.3-13.7) years for CFC-11, CFC-12, CFC-113, methyl chloroform, and HCFC-22, respectively (black lines). Uncertainties in calculated mixing ratios (shaded gray area) were derived from the lifetime ranges indicated, uncertainties in model parameters, and uncertainties in industry emissions estimates. No calculated mixing ratios are shown for carbon tetrachloride because an independent record for historic production and emission of this gas is lacking. For CFC-113 mixing ratios have also been calculated (black dashed line) based on global emission estimates by Fisher et al. (1994); corresponding calculations for the other gases are not shown because the results differ by less than 1% from the latest results.

SOURCE GASES

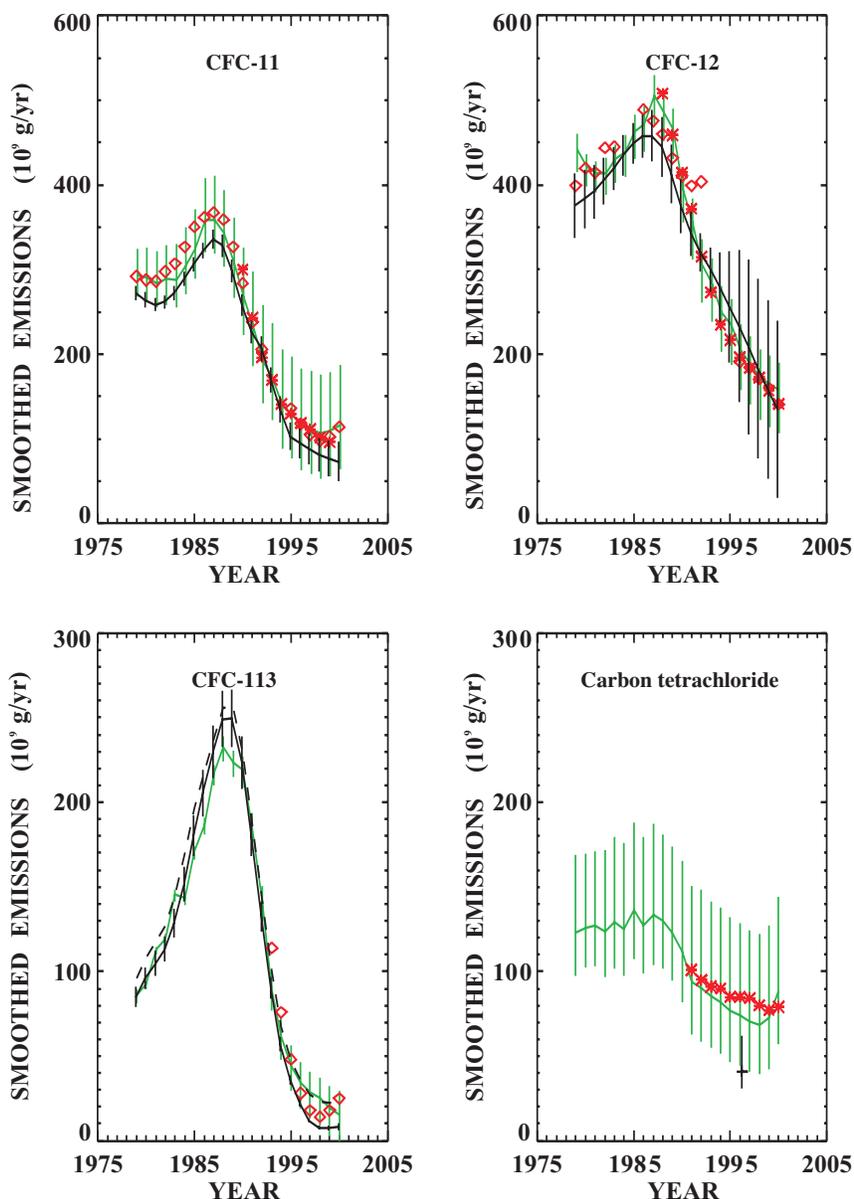


Figure 1-14. Estimates of annual emissions from industry (full black lines: based upon data from AFEAS (2001) and UNEP (2002); see Section 1.3) and inferred from measurements (green lines and red symbols) for CFC-11, CFC-12, CFC-113, and carbon tetrachloride. Uncertainties on industry emissions for CFC-11 are from McCulloch et al. (2001); for CCl_4 , see UNEP (1998b) and McCulloch et al. (2002). The black dashed line for CFC-113 indicates previous global emissions estimates that included an allotment from companies not reporting to AFEAS (Fisher et al., 1994). The only available global emission estimate for CCl_4 derived from industry data was made by UNEP (1998b) for 1996 and is indicated by a black symbol. Release estimates based on atmospheric measurements by AGAGE (green lines: Prinn et al., 2000) were made with a 12-box model (Cunnold et al., 1997) and lifetimes of 45 (29-76), 100 (77-185), 85 (54-143), and 26 (17-36) years for CFC-11, CFC-12, CFC-113, and carbon tetrachloride, respectively. The effect of these lifetime uncertainties, which were derived from an ensemble of model calculations reported in WMO (1999), and, for CCl_4 , uncertainty in the oceanic loss (Yvon-Lewis and Butler, 2002), is indicated by the green error bars. Emission estimates derived using the same AGAGE model applied to CMDL (Montzka et al., 1999) flask sample measurements (red diamonds) and CMDL in situ measurements (red asterisks) are also shown. All emission estimates derived from atmospheric measurements have been smoothed over 3-yr intervals to reduce the effects of measurement imprecision. Units of emission are 10^9 g yr^{-1} (10^9 g = 1 Gg).

estimated to be 26 (17-36) years, or about 25% shorter than in Prinn and Zander et al. (1999) (see Section 1.4.2). Emissions estimated for 1996 by TEAP (UNEP, 1998b) are below those inferred from measured trends and this lifetime (Figure 1-14), and suggest that either (1) releases of CCl_4 are higher than estimated, or (2) the current, best-estimate lifetime is too short (Figure 1-14). Calibration differences are too small to account for these large discrepancies (Table 1-1).

Uncertainties in lifetime estimates for CCl_4 are significant and account for much of the uncertainty range shown in Figure 1-14. Some insights into emissions of CCl_4 can be gleaned from a study of their relationship to CFC production, which was believed to account for the majority of carbon tetrachloride emissions (Simmonds et al., 1998a). The molar ratio, [total global CCl_4 emissions]/[total global production of CFC-11 and CFC-12], ranges between 0.12 and 0.16 during 1978-1993 when the global CCl_4 emissions are inferred from atmospheric measurements using a lifetime of 26 years (see Figure 1-15). Some fraction of global CCl_4 emissions, however, arises from processes not related to CFC production; TEAP (UNEP, 1998b) estimated that fraction at 30% in 1996. Such emissions, if included as a constant in other years, suggest fugitive emissions of CCl_4 arising from CFC production of $11 \pm 0.6\%$ during 1978-1993. After 1993 as global CFC production declines, however, this ratio increases dramatically (Figure 1-15). Such a change suggests either that fugitive releases of CCl_4 during CFC production have increased by a factor of between 1.5 and 2 in recent years, or that CCl_4 emissions not related to CFC production are much higher than previously realized.

1.6.1.4 HCFCs

In the past there have been large discrepancies between measured and calculated mixing ratios of HCFC-142b and, to a lesser extent, HCFC-141b (Montzka et al., 1994; Oram et al., 1995; Simmonds et al., 1998b). New industry-based emission estimates (see Section 1.3; AFEAS, 2001), however, result in much better agreement for HCFC-142b (Figures 1-16 and 1-17). For HCFC-142b and -141b, emissions inferred from measurements are still slightly larger than the industry estimates, whereas for HCFC-22 the industry releases appear to be on the high side, and a somewhat shorter lifetime (more OH) would result in a better fit. The incorporation of the time-dependent OH field derived by Prinn et al. (2001) worsens the differences between industry-derived emissions and those calculated from atmospheric observations of HCFC-22 (Figure 1-16). The effect of these potential OH changes on the other HCFC plots is negligible, and is not shown.

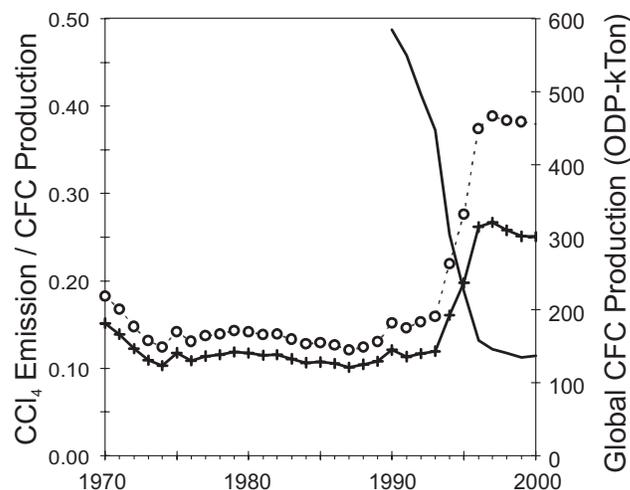


Figure 1-15. The molar ratio of global carbon tetrachloride emissions relative to aggregated CFC-11 and -12 global production (dashed line with open circles; left axis scale). In an attempt to better describe the fraction of CCl_4 emissions resulting from CFC production, this ratio is calculated alternatively by subtracting 22 Gg of CCl_4 emissions for all years (solid line with crosses; left axis scale) based upon UNEP (1998b) estimates that 30% of CCl_4 emissions in 1996 were unrelated to CFC production in 1996 (UNEP, 1998b). In this analysis global emissions for carbon tetrachloride were inferred from measurements (Prinn et al., 2000; Montzka et al., 1999) presuming a 26-yr global lifetime (Yvon-Lewis and Butler, 2002; Section 1.4.2). Also shown is the global aggregated CFC-11 and CFC-12 production in recent years (thin black line, right axis scale; UNEP, 2002).

1.6.1.5 HALONS

In the previous Assessment (WMO, 1999), substantial differences were noted between measured trends and mixing ratios of Halon-1211 and those derived from production data and release functions (Fraser et al., 1999; Butler et al., 1998). Since then TEAP (an update to UNEP, 1999) has made global estimates of emissions for both Halon-1211 and -1301 from independently derived functions that relate production to emission. For both halons, mixing ratios calculated from these two emissions histories are substantially different but provide a better picture of the uncertainties involved with this calculation than were possible previously (Figure 1-17). Fairly significant differences are also apparent in results from different laboratories for both halons: inter-laboratory differences range up to 15% for Halon-1211 and 30% for Halon-1301.

SOURCE GASES

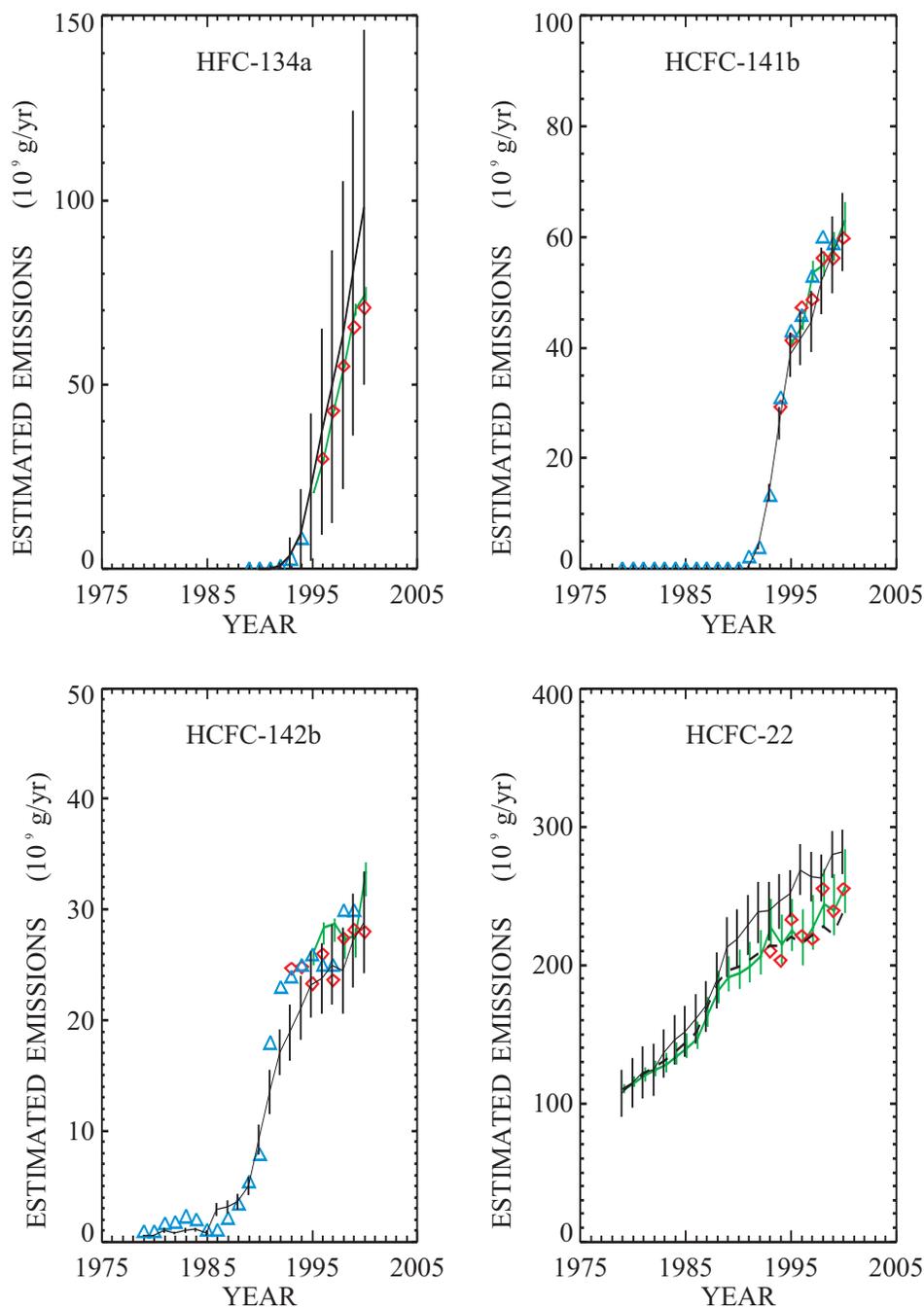


Figure 1-16. Estimates of emissions from industry (solid black lines) and inferred from measurements (green lines, red and blue symbols) for the most abundant HCFCs and HFC-134a. The green lines indicate global release estimates from measurements at one to three sites and the AGAGE model (Cunnold et al., 1997; Prinn et al., 2000; Miller et al., 1998) using global lifetimes of 14.0 years for HFC-134a, 9.3 years for HCFC-141b, 17.9 years for HCFC-142b, and 12.0 years for HCFC-22. The effect of an uncertainty of $\pm 14\%$ in the tropospheric lifetime of these compounds due to hydroxyl (see Prinn et al., 2001) is indicated by the green error bars. The red diamonds are annual release estimates obtained using the same AGAGE model applied to CMDL flask measurements (7-8 sites; Montzka et al., 1999). The blue triangles are estimates obtained from an independent set of measurements (at 41°S only) and a separate model (UEA: Oram et al., 1995, 1996). The black dashed line on the HCFC-22 panel indicates emissions inferred from AGAGE measurements with the time-dependent OH burden suggested by Prinn et al. (2001). Units of emission are 10^9 yr $^{-1}$ (10^9 g = 1 Gg).

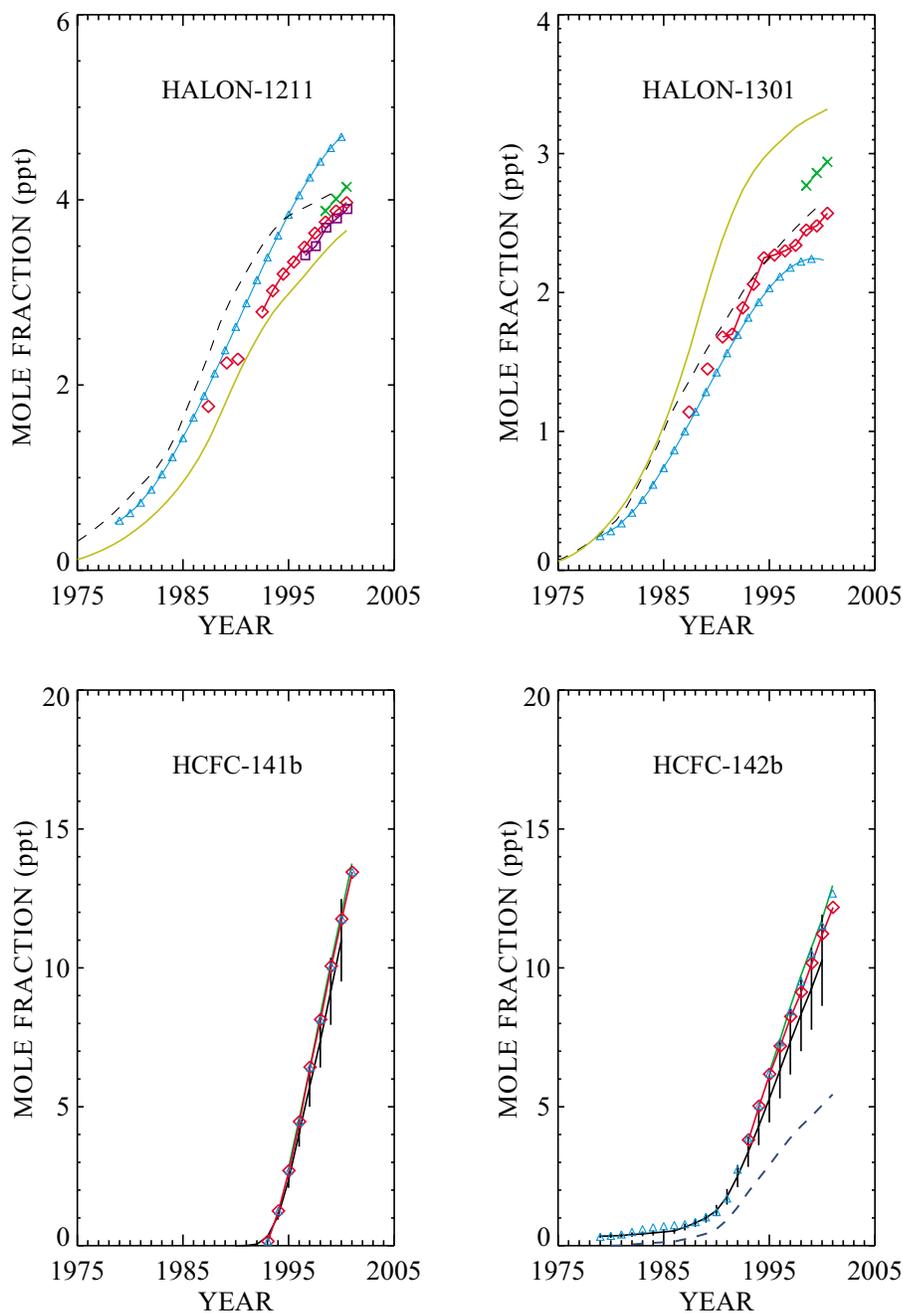


Figure 1-17. Observed and calculated global mean surface mixing ratios for selected halons and HCFCs over time. Observations are global means from CMDL flask measurements (open red diamonds: Butler et al., 1998; Montzka et al., 1999); global means from AGAGE in situ instruments (green crosses or solid green lines: Prinn et al., 2000; Sturrock et al., 2001); global means from UCI quarterly flask measurements (open purple squares: Blake et al., 2001, Halon-1211 only); and global means derived from an analysis of the Cape Grim Air Archive by UEA (blue triangles: Fraser et al., 1999; Oram et al., 1995). Mixing ratios were calculated with 2-D models and lifetimes of 17 years for Halon-1211 and 62 years for Halon-1301 (Fraser et al., 1999), 9.3 yrs for HCFC-141b, and 17.9 years for HCFC-142b. Mixing ratios calculated with emissions of halons derived from industry production data are from Fraser et al. (1999) (black dashed lines, halons only) and updated UNEP (1999) (gold line). Mixing ratios of HCFCs are calculated from a combination of AFEAS (2001) and UNEP (2002) emissions with updated release functions for HCFC-142b from foams (black lines; see Section 1.3), and, for comparison, with the older release function for HCFC-142b from foams (dashed blue line, HCFC-142b panel only).

SOURCE GASES

Within these rather large uncertainties there is broad consistency between calculated and observed mixing ratios for both halons.

1.6.1.6 REGIONAL EMISSIONS

Initially using a simple long-range transport model (Simmonds et al., 1996) and more recently a Lagrangian dispersion model (Ryall et al., 2000), the European emission source strengths required to support the AGAGE observations of pollution episodes at Mace Head, Ireland, have been determined (see Table 1-11). Simmonds et al. (1996) compared the pre-1995 estimates with industry-derived emission estimates for Europe. They showed agreement of the values within a factor of 2 and, in particular, roughly similar declines in the emissions from 1987 to 1994. These studies demonstrated the almost complete phaseout of European emissions of methyl chloroform and CFC-113. Although the releases of CFC-11 and -12 have dramatically declined, by more than a factor of 10, European emissions of these gases are still continuing at detectable and non-negligible levels. The contributions of source regions to Mace Head fall off rapidly to the east and south, with contributions falling by more than 3 orders of magnitude toward the eastern Mediterranean, which is a result of both fewer transport events to Mace Head and greater dilution during transport to Mace Head (Ryall et al., 2000).

1.6.2 Are Atmospheric Measurements Consistent with Compliance with the Fully Amended Montreal Protocol?

Atmospheric measurements can provide an indirect and independent assessment of production and consumption data reported to UNEP. This assessment can then be considered in light of the magnitude of known production reported to UNEP and limits to production and consumption outlined in the Montreal Protocol. Significant uncertainties in this approach arise from uncertainties in measurements and trace gas lifetimes, in model calculations of mixing ratios and emissions, and in the release functions that relate emissions to industry production data.

Global measurements can provide estimates of global emissions (Figures 1-14 and 1-16) and hence an indication of the accuracy of global production and consumption data, but this analysis addresses compliance only for ODSs that are restricted worldwide. Through 2001, limits to production and consumption of ODSs in both developed and developing countries applied only to CFCs. By 2005, global limits to production and consumption by Parties to the Protocol will apply also to halons, methyl chloroform, carbon tetrachloride, and methyl bromide.

Global production of ODSs declined dramatically during the 1990s because of limits set by the Protocol on production in developed (non-Article 5(1)) countries where most ODSs had occurred. In the data reported to UNEP, production in non-Article 5(1) countries was below the allowable limits throughout the 1990s (Figure 1-18).

As mentioned above, global limits apply only to CFC production and consumption at the present time; reported global production in 1999 was less than the allowed consumption during that year by about 20×10^3 ODP-tons. Measurements of all three major CFCs suggest 5-10% higher mixing ratios than expected based on reported global production in 1999 (Figure 1-13). These elevated mixing ratios do not necessarily imply additional unreported production of these gases in 1999; for CFC-11 and -12, the mismatch is present throughout the entire measurement period and unaccounted-for emissions in recent years cannot explain this discrepancy. In fact, observed and calculated mixing ratios for CFC-12 have been converging during the 1990s, indicating that emissions estimated by industry since 1995 may be overestimates by an average of about 30×10^3 ODP-tons yr^{-1} (or 30 Gg; Figure 1-14), consistent with improved containment in recent years (UNEP, 1998a). For CFC-113 good consistency is observed until the beginning of the 1990s. After that a small divergence becomes apparent. This mismatch could be reconciled with about 10×10^3 ODP-tons of additional CFC-113 emission in recent years. If the small discrepancies for CFCs noted here were all attributed to errors in reported production, the measured atmospheric trends would suggest slightly less aggregate CFC production in the late 1990s than reported to UNEP. CFC production reported to UNEP in 1999 was somewhat ($\sim 20 \times 10^3$ ODP-tons) below the Montreal Protocol limit for that year (UNEP, 2002); the atmospheric measurements are not inconsistent with this assertion.

For halons, production data reported to the UNEP Ozone Secretariat for 1995-1999 are similar to the global limit that will apply beginning in 2002. If the trends indicated by the data in 1998 and 1999 persist into the future, production would be quite below the limits allowed in 2002 (Figure 1-18). Assessing the accuracy of reported production with atmospheric measurements for halons (Figure 1-17) is difficult because of the rather large uncertainties in measurement calibration, in the relation between production and emission for halons, and in the atmospheric lifetime for Halon-1211. Within these rather large uncertainties the atmospheric observations are broadly consistent with known production reported to UNEP for both Halon-1211 and Halon-1301.

Table 1-11. European emission source strengths required to support the AGAGE observations of each halocarbon and greenhouse gas at Mace Head, Ireland, over the period 1987-2000 (emissions in thousand tons per year).

Year	CFC-11	CFC-12	CFC-113	CH ₃ CCl ₃	CCl ₄	CHCl ₃	CH ₄	N ₂ O
1987	215	153	68	207	27		47 900	2 200
1988	132	98	43	115	20		22 500	1 800
1989	94	87	63	159	26		22 700	1 300
1990	67	64	63	153	12		31 500	1 800
1991	52	59	44	108	14		35 200	2 700
1992	27	32	31	88	9		31 000	1 600
1993	20	22	21	75	6		23 600	1 600
1994	25	31	20	115	5		40 900	2 400
1995	9	15	5	31	3	20	24 800	1 400
1996	8	14	4	19	4	15	27 800	1 500
1997	9	13	2	8	3	19	27 300	1 700
1998	10	13	2	2	3	20	25 800	1 600
1999	9	11	1	0	2	19	32 000	1 600
2000	6	6	1	0	1	16	20 500	1 000
	HCFC-141b	HCFC-142b	HCFC-22	HFC-134a	HFC-152a			
1995	8	6	23	3	0.4			
1996	9	6	20	6	0.5			
1997	13	9	34	11	0.7			
1998	14	8						
1999	12	8	29	13	1			
2000	9	4	20	10	0.7			

A simple long-range transport model (Simmonds et al., 1996) was employed for the 1987-1994 period and a Lagrangian dispersion model (Ryall et al., 2000) thereafter.

For carbon tetrachloride, difficulties have arisen in reporting appropriate data to UNEP (UNEP, 1998b). In light of this, limits to production and consumption are compared with *emissions* derived from measurements rather than consumption or production data reported to the UNEP Ozone Secretariat (Figure 1-18). For most uses, emissions of CCl₄ closely follow sales, so this approach can yield some insight. Global limits on CCl₄ production apply only after 2005, so it is not meaningful to ask if atmospheric measurements suggest compliance until after that date. Inferred emissions in 1999, however, are about 7 times greater than the limits to global production set for 2005.

For methyl chloroform, global production reported in 1999 was substantially lower than the limit for non-Article 5(1) countries. In addition, production in 1999 was already comparable with the global production limit for 2002.

For HCFCs, limits to global production apply only after 2015. Global production is below the current consumption limit for non-Article 5(1) countries (Figure 1-18).

1.7 OTHER TRACE GASES

1.7.1 Carbon Dioxide (CO₂)

Changes in climate and meteorological conditions affect the ozone layer, because ozone depletion and climate change share common physical and chemical processes. Anthropogenic carbon dioxide (CO₂) is the major contributor to the increase in radiative forcing from trace gas changes since preindustrial times. For this reason, atmospheric CO₂, the global carbon cycle, and mankind's impacts on them through such activities as fossil fuel combustion and changes in land use are addressed in considerable detail in Chapter 3 of the IPCC *Climate Change 2001* report (Prentice et al., 2001). Similarly, the 2001 IPCC *Special Report on Emissions Scenarios*, or SRES (Nakićenović et al., 2000) presents a wide range of projected emissions of CO₂ and other radiatively important trace gases over the coming century. We present here only a very brief overview of the main points, and we refer the reader to those IPCC reports for detailed discussions and references.

SOURCE GASES

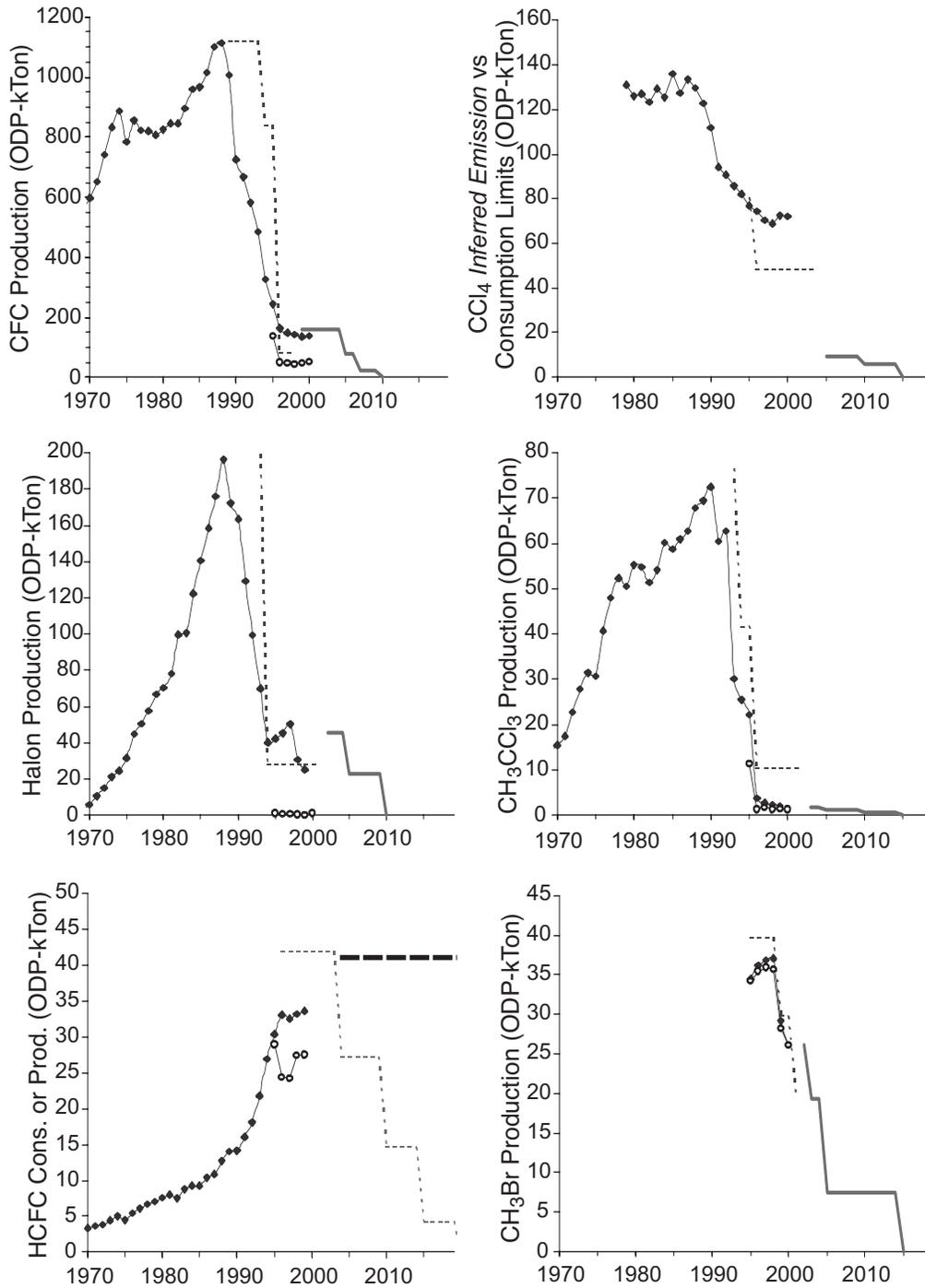


Figure 1-18. A comparison between reported global ODS production (filled solid diamonds with connecting lines: AFEAS, 2001; UNEP, 2002); ODS production reported in non-Article 5(1) countries (open circles with connecting lines: UNEP, 2002); and global ODS production limits (thick solid lines) as outlined in the fully revised and amended Montreal Protocol. Also shown are production or consumption limits for non-Article 5(1) countries in years before global limits apply (short-dashed lines). For CCl₄, global emissions inferred from measurements are shown instead of reported global production. For HCFCs, global limits to production and consumption apply only after 2015, so the non-Article 5(1) consumption limit (short-dashed lines) and production limit (thick long-dashed line) are shown instead. For some ODSs, global production in the late 1990s is higher than non-Article 5(1) limits because significant amounts were produced in countries operating under Article 5(1) during those years.

The atmospheric burden of CO₂ has increased by about 35% since 1750, to a mean abundance of ~370 parts per million (ppm) in 2000 (Table 1-12). Systematic measurements of atmospheric CO₂ since the late 1950s show a regular increase, with a mean growth rate at Earth's surface of ~1.5 ppm yr⁻¹ (0.4% yr⁻¹) over the past two decades (Figure 1-19; Tans et al., 2002). This increase is roughly half of that expected from the combustion of fossil fuels and cement production, the difference being due to CO₂ uptake by the oceans and by the terrestrial biosphere. There is considerable interannual variability in this rate of increase that is due to the effects of climate variability (e.g., El Niño events) on these uptake processes (Battle et al., 2000; Le Quere et al., 2002). This variability is also shown by measurements of total CO₂ column abundances above the Jungfraujoch (Zander et al., 2002).

CO₂ from fossil fuel burning will continue to be the dominant factor determining atmospheric CO₂ levels during the 21st century. Among the six emissions scenarios considered by the SRES (Nakićenović et al., 2000), the projected range of CO₂ abundances in 2100 was between 540 and 970 ppm, substantially higher than present-day amounts (Figure 1-19). Among the largest uncertainties in these projections are the effects of climate change on rates of deep ocean mixing, as well as on surface ocean and terrestrial biological productivity.

1.7.2 Methane (CH₄)

Atmospheric methane (CH₄) is a greenhouse gas whose radiative properties and atmospheric chemistry affect both climate and stratospheric ozone. Because methane is a sink for reactive chlorine and a source of H₂O vapor, it directly influences the availability of inorganic halogen for depleting stratospheric ozone. Furthermore, the atmospheric chemistry of methane affects hydroxyl radical (OH) abundance on global scales. This can alter degradation rates (lifetimes) of methane and ozone-depleting substances such as methyl chloroform and HCFCs. Finally, methane affects climate. Hansen and Sato (2001) estimate a change in radiative forcing for CH₄ in 2000 compared with preindustrial time, including direct and indirect effects, of $0.7 \pm 0.2 \text{ W m}^{-2}$, which is one-half the change in forcing due to CO₂ increases.

Although global concentrations of methane have varied in preindustrial times, amounts present in today's atmosphere are thought to be higher than at any time in the past 420,000 years. Whereas the globally averaged methane mole fraction in 2000 was estimated to be between 1752 ppb (updates of Dlugokencky et al., 2001) and 1784 ppb (AGAGE network, Tohoku University gravimetric scale; Cunnold et al., 2002) (Table 1-12),

measurements of CH₄ in air extracted from polar ice indicate that its abundance during the last 420,000 years of the preindustrial era varied between about 350 ppb during glacial times and about 700 ppb during interglacial periods (Petit et al., 1999). From ice-core measurements in Antarctica and Greenland, and Antarctic firn and archived air from southern midlatitudes, Etheridge et al. (1998) showed that the globally averaged methane mole fraction was relatively constant at 695 ppb from 1000 to 1800 A.D., and increased through the industrial era.

Systematic measurements of atmospheric CH₄ show that its global abundance at Earth's surface continues to increase (Figure 1-19); the average growth rate was $7.9 \pm 0.1 \text{ ppb yr}^{-1}$ from 1984 to 2000, and the rate of increase slowed from about 14 ppb yr^{-1} in the early 1980s to less than 5 ppb yr^{-1} in the late-1990s (except during 1998). The 1999-2000 global growth rate was less than 2 ppb yr^{-1} (Table 1-12). Significant interannual variability is superimposed on the long-term decrease in growth rate (Dlugokencky et al., 1998, 2001; Simpson et al., 2002; Cunnold et al., 2002). Monitoring of the vertical column abundance of CH₄ above the Jungfraujoch since the mid-1980s also confirms the continued slowing of the rate of CH₄ accumulation in the atmosphere, which was found equal to 0.72% in 1987-1988, 0.51% in 1991-1992, 0.32% in 1995-1996, and 0.14% in 1999-2000 (Zander et al., 2002).

The cause of the decrease in methane growth rate is not fully understood. Although the major sources of atmospheric methane are known, they are poorly quantified. Bottom-up assessments from individual sources of emission rates and their changes over time are not reliable enough to discern small changes in global emission rates. Changes in hydroxyl radical abundance also would affect methane growth rates, but much uncertainty remains regarding trends of this important atmospheric oxidant (see Section 1.4; Krol et al., 1998; Prinn et al., 2001). Dlugokencky et al. (1998) have suggested that the recent methane trends can be explained by an approach of the system to steady state, i.e., fairly constant emissions and lifetime in recent years. Resolution of these issues has important implications for projecting future concentrations.

IPCC (Prather and Ehhalt et al., 2001) calculated future CH₄ abundances from 2000 to 2100 based on CH₄ emission rates in the six illustrative scenarios in the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-19). By 2100, CH₄ mixing ratios range from about 1575 ppb (i.e., 10% below present-day mixing ratios; 1880 ppb in 2050) for IPCC scenario B1, which emphasized relatively small global population and resource-efficient technologies, to 3730 ppb (2560 ppb in 2050) for scenario E0 (not shown in Figure 1-19), which

SOURCE GASES

Table 1-12. Mixing ratios and growth rates for HFCs, FCs, sulfur hexafluoride, nitrous oxide, methane, carbon dioxide, and carbon monoxide.

Species	Common or Industrial Name	Mixing Ratio			Growth (1999-2000)		Laboratory (No. of sites), Method
		1996	1998	2000	ppx yr ⁻¹	% yr ⁻¹	
HFCs (ppt)							
CHF ₃	HFC-23	11.7	13.5	15.5	0.9	5.8	UEA, SH (1), flask ^a
CHF ₂ CF ₃	HFC-125		0.92	1.4	0.3	22	AGAGE (2), in situ ^a
CH ₂ FCF ₃	HFC-134a		7.9	14.6	3.5	27	AGAGE (2), in situ ^a
		3.0	7.6	13.8	3.2	26	CMDL (8), flask ^a
CH ₃ CHF ₂	HFC-152a		1.3	1.7	0.2	12	AGAGE (2), in situ ^a
FCs (ppt)							
CF ₄	FC-14		76.0				MPAE, NH (1), flask ^a
CF ₃ CF ₃	FC-116	2.2					UEA, SH (1), flask ^a
c-C ₄ F ₈	FC-318	1.0					UEA, SH (1), flask ^a
SF ₆ (ppt)	Sulfur hexafluoride	3.5	3.9				UH, SH (1), flask ^b
		3.6					UEA, SH (1), flask ^a
		3.8	4.3	4.7	0.21	4.6	CMDL (7), flask ^b
			4.2	4.6	0.18	4.0	CMDL (5), in situ ^b
N ₂ O (ppb)	Nitrous oxide	312.7	314.1	316.0	1.0	0.32	AGAGE (4-5), in situ ^b
		312.0	313.8	315.7	0.85	0.27	CSIRO, SH (1), flask ^b
		312.2	313.2	315.2	1.0	0.32	CMDL (7), flask ^b
		312.7	314.3	317.2	1.1	0.35	CMDL (5), in situ ^b
CH ₄ (ppb)	Methane	1761.7	1774.7	1784.4	1.3	0.07	AGAGE (4-5), in situ ^c
		1681.3	1695.8	1707.6	1.7	0.10	CSIRO, SH (1), flask ^c
		1729.7	1743.2	1751.6	0.7	0.04	CMDL (42), flask ^c
		1751.2	1764.7	1771.1	2.1	0.12	UCI (~40), flask ^c
CO ₂ (ppm)	Carbon dioxide	361.6	365.4	368.6	1.1	0.31	CMDL (44), flask ^{d,*}
CO (ppb)	Carbon monoxide	112.1	144.5	112.2	-11.6	-9.9	AGAGE, NH (2-3), in situ ^e
		110.8	132.1	106.0	-13.5	-12.3	CMDL, NH (24), flask ^e
		52.3	56.4	51.0	-2.3	-4.4	AGAGE, SH (2), in situ ^e
		50.8	56.2	50.6	-2.2	-4.2	CSIRO, SH (1), flask ^e
		54.3	60.3	55.9	-1.8	-3.2	CMDL, SH (19), flask ^e

Global mixing ratios (dry air mole fractions) and growth rates are at Earth's surface unless otherwise specified as being from Northern Hemisphere (NH) or Southern Hemisphere (SH) sites only. Laboratories: Advanced Global Atmospheric Gases Experiment (AGAGE); Global Atmospheric Sampling Laboratory, Commonwealth Scientific and Industrial Research Organization (CSIRO), sampling at 41°S; Max-Planck-Institut für Aeronomie (MPAE), sampling at Lindau, Germany; Climate Monitoring and Diagnostics Laboratory (CMDL), National Oceanic and Atmospheric Administration (NOAA); University of East Anglia (UEA), sampling at 41°S; University of Heidelberg (UH), sampling at 41°S; University of California at Irvine (UCI), quarterly sampling at about 40 sites.

Data sources: AGAGE: Prinn et al. (2000); Cunnold et al. (2002); ftp://cdiac.esd.ornl.gov/pub/ale_gage_Agage. CMDL: Dlugokencky et al. (2001); Montzka et al. (1996b); Novelli et al. (1998); Tans et al. (2002); www.cmdl.noaa.gov. CSIRO: Langenfelds et al. (2002). MPAE: Harnisch et al. (1999). UEA: Oram et al. (1998); Oram (1999). UCI: Simpson et al. (2002). UH: Maiss and Brenninkmeijer (1998).

* Many other groups measure CO₂; only results from the most extensive network are included here (see Prentice et al., 2001).

^a Measurements by gas chromatography-mass spectrometric detection.

^b Measurements by gas chromatography-electron capture detection.

^c Measurements by gas chromatography-flame ionization detection.

^d Measurements by nondispersive infrared detection.

^e Measurements by gas chromatography-mercuric oxide reduction detection.

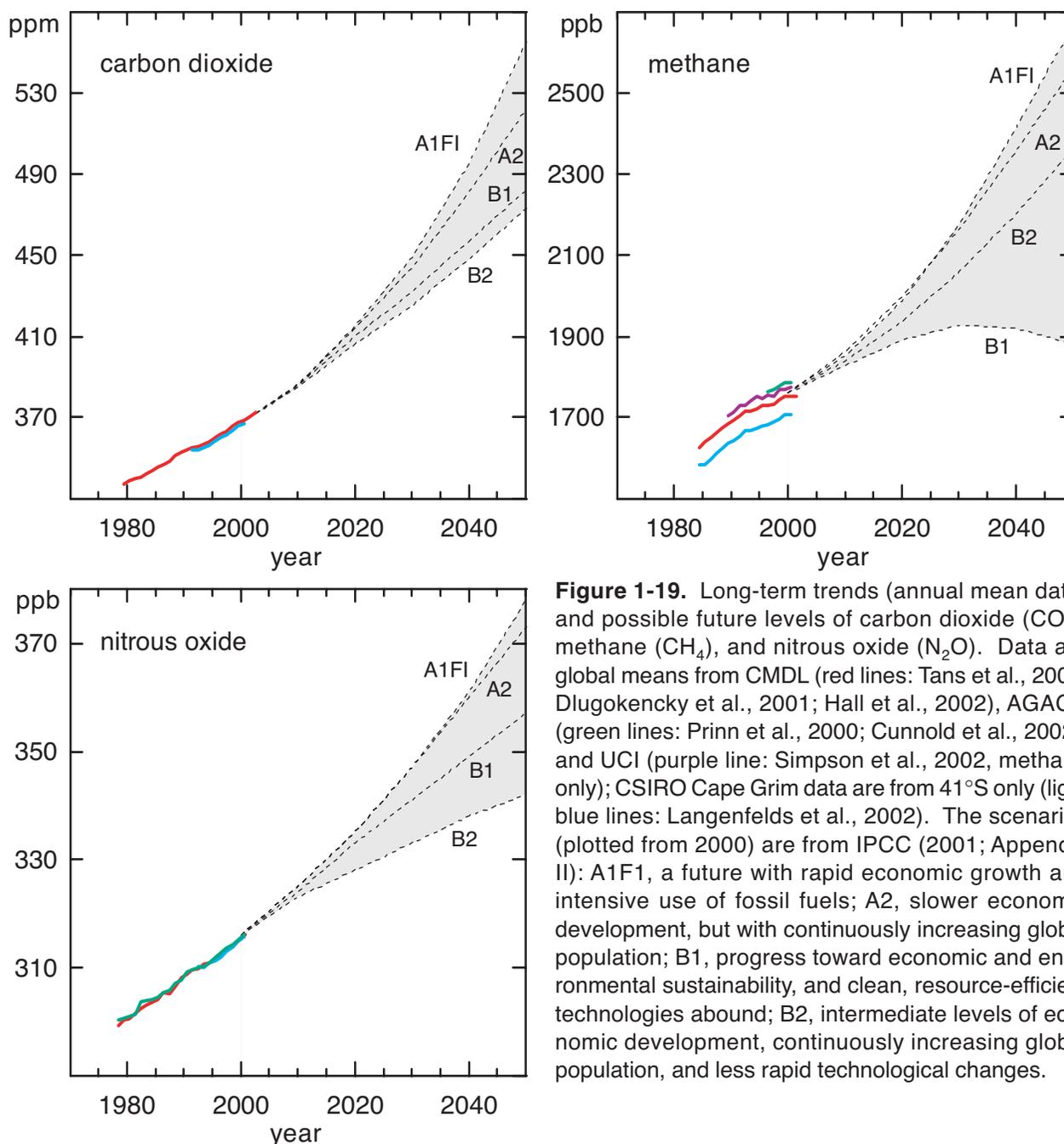


Figure 1-19. Long-term trends (annual mean data) and possible future levels of carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O). Data are global means from CMDL (red lines: Tans et al., 2001; Dlugokencky et al., 2001; Hall et al., 2002), AGAGE (green lines: Prinn et al., 2000; Cunnold et al., 2002), and UCI (purple line: Simpson et al., 2002, methane only); CSIRO Cape Grim data are from 41°S only (light blue lines: Langenfelds et al., 2002). The scenarios (plotted from 2000) are from IPCC (2001; Appendix II): A1F1, a future with rapid economic growth and intensive use of fossil fuels; A2, slower economic development, but with continuously increasing global population; B1, progress toward economic and environmental sustainability, and clean, resource-efficient technologies abound; B2, intermediate levels of economic development, continuously increasing global population, and less rapid technological changes.

included rapid population growth through the century and regional solutions to environmental problems. Though the range of values is large, the scenarios provide a range of potential future atmospheric composition for given amounts of CH₄ emissions.

1.7.3 Nitrous Oxide (N₂O)

Nitrous oxide (N₂O) is the major source of ozone-depleting nitrogen oxides (NO_x) in the stratosphere. These

reaction products of N₂O photochemistry make a significant contribution to both anthropogenic and natural ozone depletion. New rate constants for some stratospheric reactions indicate an enhanced role for NO_x in ozone loss (Portmann et al., 1999). Consequently, it is possible that enhanced future N₂O emissions could noticeably delay stratospheric ozone recovery (Randeniya et al., 2002).

The atmospheric burden of N₂O has been increasing steadily for decades (Figure 1-19). NOAA/CMDL and AGAGE data show that the globally averaged

SOURCE GASES

mixing ratio in January 2001 was 315-317 ppb (Prinn et al., 2000; Hall et al., 2002). Its rate of increase has averaged ~ 0.75 ppb yr^{-1} , with some interannual variability since the late 1970s. Its lifetime is currently estimated at 120 (97-137) years, although its “perturbation” lifetime is 4-6% shorter (Prather, 1998).

Most updates in our understanding of the sources and sinks of atmospheric N_2O since the 1998 Assessment (WMO, 1999) were assessed in Chapter 4 of the Third Assessment Report (TAR) for the IPCC (Prather and Ehhalt et al., 2001). A number of studies discussed in that report show a preindustrial tropospheric abundance of N_2O of ~ 270 ppb, suggesting an increase in the atmospheric burden of about 17% since then. Little has changed in our overall understanding of the atmospheric budget of this gas since the 1998 Assessment. Known sources of 15-18 Tg yr^{-1} , mainly from natural soils, agricultural activities, biomass burning, and the ocean, can be accounted for by known sinks and observed increases. However, the uncertainties in the source estimates are large. The suggested need for a large stratospheric or exotic source of N_2O to account for the isotopic composition of the troposphere has been found by a number of studies not to be necessary (Prather and Ehhalt et al., 2001).

1.7.4 Carbon Monoxide (CO)

In the troposphere, carbon monoxide (CO) is closely linked to the cycles of ozone and methane, and plays an important role in the control of the OH radical concentration. Hydroxyl radical, in turn, controls the lifetime of many reduced compounds (e.g., CH_4 , HCFCs, HFCs, and CH_3CCl_3). Therefore, predicting future concentrations of these ozone-relevant and radiatively important gases depends partly on how well the CO budget and its potential for change is understood. CO could be assigned a GWP because of its effect on the lifetime of other greenhouse gases (e.g., Prather, 1996; Daniel and Solomon, 1998; Prather and Ehhalt et al., 2001). In this regard, emitting 100 Tg of CO is equivalent to emitting 5 Tg of CH_4 (Wild and Prather, 2000; Derwent et al., 2001). Most budgets evaluated by Prather and Ehhalt et al. (2001) estimate a current annual source of CO to the troposphere in the range of 2000 to 3000 Tg.

1.7.4.1 ATMOSPHERIC GLOBAL DISTRIBUTION AND TRENDS

Modern direct measurements indicate that trends in atmospheric CO were positive until the mid- to late-1980s at least in the Northern Hemisphere, but since then the mean trend has been negative (Zander et al., 2000; Khalil and Rasmussen, 1994; Mahieu et al., 1997; Novelli

et al., 1998), e.g., reaching a decrease of -0.6% yr^{-1} above the Jungfraujoch in 1999-2000 (Zander et al., 2002). CO exhibits both short- and long-term changes on regional and global scales and, after an overall increase over several decades, it appears that CO has declined in many parts of the world (Table 1-12; see also Kurylo and Rodríguez et al., 1999). Causes of these recent changes have not been identified with certainty, but decreases in tropical biomass burning (Yung et al., 1999), decreases in Northern Hemispheric urban emissions (Bradley et al., 1999), and increases in OH concentrations due to stratospheric ozone depletion (Krol et al., 1998; Law, 1999) may have played a role (although one study suggests *decreases* in OH in the 1990s (Prinn et al., 2000)). Short-term increases in CO column abundances and surface mixing ratios were observed during the strong El Niño of 1998, probably as a result of enhanced burning then (Wotawa et al., 2001; Rinsland et al., 2000). No long-term change has been detected in CO mixing ratios at Cape Point, South Africa, during 1978-1998 (Scheel et al., 1995).

1.7.4.2 CO SOURCES AND SINKS

CO has significant atmospheric photochemical sources from the oxidation of CH_4 and non-methane hydrocarbons, as well as emissions from fuel combustion and biomass burning. Considerable uncertainties exist in the CO budget. Recent evaluations of global sources and budget suggest that the principal sources are biomass burning, fossil fuel combustion, agricultural waste burning, biofuel combustion, and industrial processes. The global surface source is estimated at 1550 Tg yr^{-1} (Prather and Ehhalt et al., 2001).

The most important sink of CO is reaction with OH. Uncertainties in OH distributions and the reaction rate constant of $\text{CO} + \text{OH}$ result in a large range of estimates for this sink. McCabe et al. (2001) have studied the kinetics of $\text{CO} + \text{OH}$ for atmospheric conditions in the laboratory, decreasing the uncertainty in the rate coefficient significantly. Atmospheric CO is consumed by soils; recent studies (Potter et al., 1996; Sanhueza et al., 1998; King, 2000) suggest global consumption by soils of 100-300 Tg yr^{-1} , lower than the 190-580 Tg yr^{-1} proposed by Conrad and Seiler (1985), which has been widely used in previous Assessment budgets.

1.7.4.3 ISOTOPIC DATA

Isotopic studies of atmospheric CO (Brenninkmeijer et al., 1999) provide an absolute technique by which atmospheric mixing ratios of CO are determined (Brenninkmeijer et al., 2001). Confirmation that CO undergoes mass-independent fractionation (Röckmann et

al., 2001) indicates that previous ^{13}C data may need a small, but significant, correction (Röckmann and Brenninkmeijer, 1998). Additional work is needed in defining fractionation of some CO production processes, notably, CH_4 and non- CH_4 hydrocarbon oxidation, and its combustion sources.

1.7.5 Carbonyl Sulfide (COS)

Carbonyl sulfide (COS) is the most abundant sulfur-containing trace gas in the atmosphere. Because it has a lifetime that is long relative to atmospheric mixing times (>1 year), much of the COS emitted or produced in the troposphere reaches the stratosphere. Some fraction of stratospheric COS becomes photolyzed and contributes sulfur to the stratospheric aerosol layer. This aerosol provides surfaces that enhance the concentration of ozone-depleting radicals; it also plays an important role in the radiative balance of the atmosphere. Earlier work had suggested that COS might be the main source of nonvolcanic sulfate to the stratosphere (Crutzen, 1976). More recent work, however, based on revised reaction rates, cross sections, and photolytic quantum yields, has suggested that COS may account for a smaller fraction of the sulfate present in the stratospheric Junge layer than previously thought (Chin and Davis, 1995; Kjellstrom, 1998; see also Chapter 2).

A combination of results from total column abundances (Rinsland et al., 2002a; Mahieu et al., 1997; Griffith et al., 1998), periodic surface measurements (Bandy et al., 1992; Thornton et al., 1996), and an analysis of firn air in both hemispheres (Sturges et al., 2001b) suggests that the atmospheric burden of COS was fairly constant from the mid-1900s to the early 1990s. In the 1990s updated results suggest a slight decrease (about $1\% \text{ yr}^{-1}$ or smaller) (Mahieu et al., 1997; Sturges et al., 2001b); Rinsland et al. (2002a) have inferred a mean tropospheric decrease from 1978 to 2002 at 32°N equal to $0.25 \pm 0.04\% \text{ yr}^{-1}$. Firn air results suggest that the recent decreases may have been more pronounced in the Northern Hemisphere than in the Southern Hemisphere (Sturges et al., 2001b); they also point to the possibility of lower COS mixing ratios in the oldest air sampled in Antarctica. Results from an Antarctic ice core suggest that preindustrial mixing ratios of COS were 25% lower than observed in the modern atmosphere (Aydin et al., 2002).

Although numerous sources and sinks of COS have been identified, much uncertainty remains regarding the magnitude of these fluxes. Until recently, best estimates of total sources outweighed sinks for COS by $\sim 30\%$, despite evidence to suggest fairly constant mixing ratios over time in the atmosphere. More recent work by Kuhn et al. (1999), Kesselmeier et al. (1999), and Simmons et

al. (1999) confirmed the earlier work of Castro and Galloway (1991) and suggests a much enhanced role for soils in the removal of COS from the atmosphere. With this new understanding of soil losses and some revision in the net influence of open and coastal oceans, Watts (2000) suggested that the magnitude of known sinks is similar to known sources despite the large uncertainties. The magnitude of sinks or sources and a mean atmospheric concentration of about 500 ppt imply a COS global lifetime of about 4 years (Chin and Davis, 1995; Watts, 2000).

1.7.6 Hydrofluorocarbons (HFCs)

The most abundant hydrofluorocarbons (HFCs) in the present-day atmosphere are HFC-23 (CHF_3) and HFC-134a (CH_2FCF_3). Since the previous Assessment, the tropospheric abundance of each has continued to increase. In addition, three more HFCs have been identified in the background atmosphere: HFC-125 (CHF_2CF_3), HFC-143a (CH_3CF_3), and HFC-152a (CH_3CHF_2). Their atmospheric mixing ratios are relatively low but are increasing at significant rates.

1.7.6.1 HFC-134a

HFC-134a (CH_2FCF_3) is used extensively as a refrigerant and air-conditioning agent, and to a lesser degree as a foam-blowing agent. Updated measurements show that the global mean surface mixing ratio of HFC-134a had risen to just under 15 ppt by mid-2000 (Table 1-12; Figure 1-20; Simmonds et al., 1998b; Montzka et al., 1999; Prinn et al., 2000; Sturrock et al., 2001). The current growth rate of about 3.0 ppt yr^{-1} has approximately doubled since 1996. Calibration differences between CMDL and AGAGE are less than 5%.

IPCC (Prather and Ehhalt et al., 2001) calculated future HFC-134a abundances from 2000 to 2100 based on HFC-134a emission rates in the six illustrative scenarios in the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-20). By 2100, HCFC-134a mixing ratios range from about 380 ppt (290 ppt in 2050) in IPCC scenario B1 to 960 ppt (535 ppt in 2050) in IPCC scenario A1.

1.7.6.2 HFC-23

Although HFC-23 (CHF_3) has found minor uses in refrigeration, plasma etching, and as a fire extinguishant, its major atmospheric source is as a byproduct from the manufacture of HCFC-22 (Oram et al., 1998). In addition, Engen et al. (1998) reported elevated levels of HFC-23 when sampling the emissions from an aluminum production plant.

SOURCE GASES

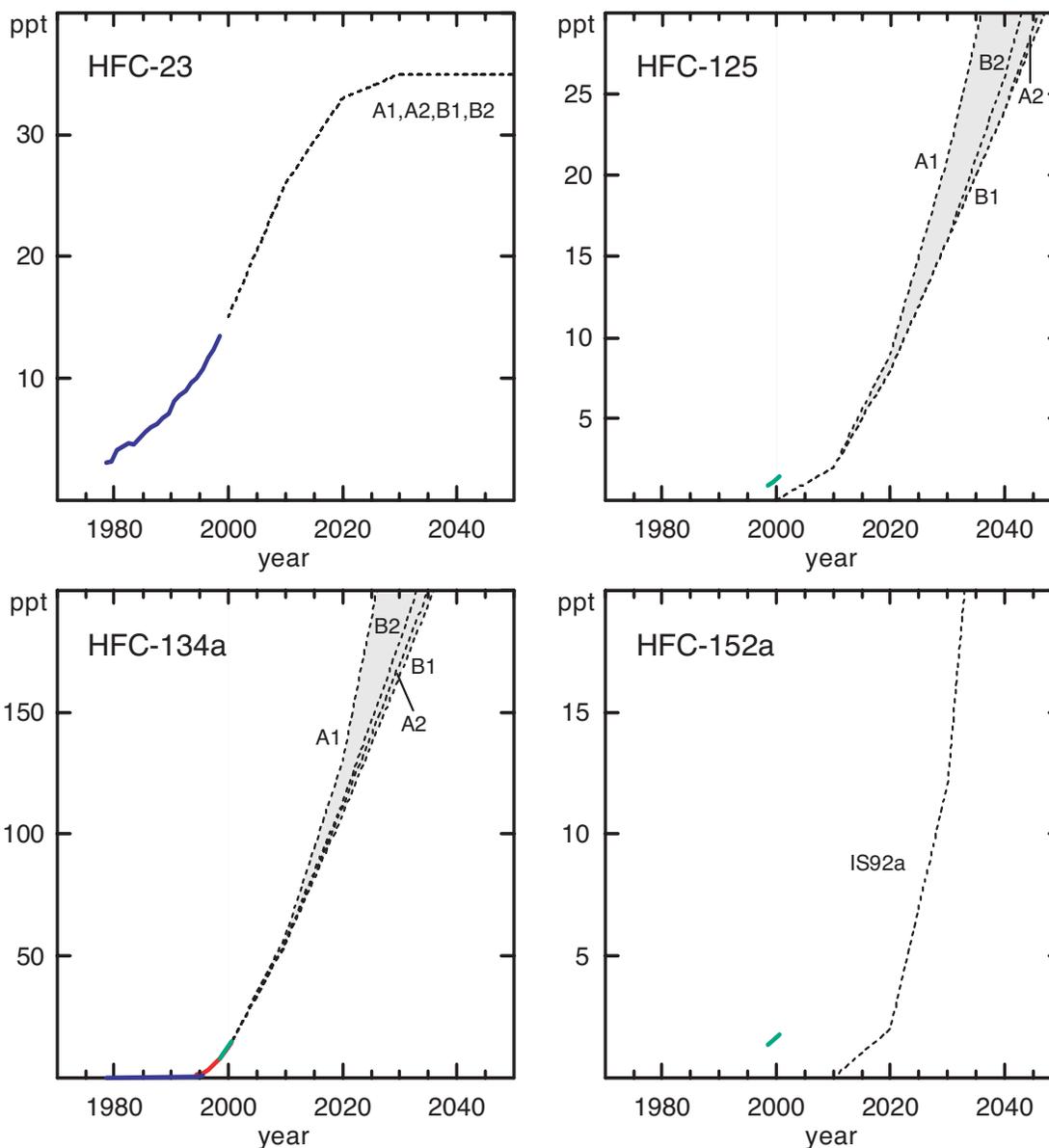


Figure 1-20. Long-term trends (annual mean data) and possible future levels of HFCs. Data are global means from CMDL (red line: Montzka et al., 1996b, HFC-134a only), and AGAGE (green lines: Prinn et al., 2000; Sturrock et al., 2001). Cape Grim results are for 41°S only (blue lines: Oram et al., 1996; 1998). The scenarios (plotted after 2000) are from IPCC (2001; Appendix II).

The only available time series of tropospheric HFC-23 measurements are those of Oram et al. (1998). The mixing ratio of HFC-23 at Cape Grim has risen from 2 ppt in 1978 to 15.5 ppt in 2000 (Table 1-12; Figure 1-20). Despite the emission reductions that have occurred in developed countries as a result of improved HCFC-22 process control and capture of the HFC-23 byproduct, the growth rate of HFC-23 at Cape Grim has increased in recent years from 0.55 ppt yr⁻¹ in 1995 to 0.9 ppt yr⁻¹ (6% yr⁻¹) in late 1999. This may have resulted from increased

HCFC-22 production in developing countries recently (McFarland and van Gerwen, 2000).

The presence of HFC-23 in the atmosphere has been confirmed by Engen et al. (1998) and Culbertson et al. (2000). In the latter study, a mean mixing ratio of 18 ± 2 ppt was measured in air samples collected at a rural, continental site in the United States in March-April 2000.

IPCC (Prather and Ehhalt et al., 2001) calculated future HFC-23 abundances from 2000 to 2100 based on HFC-23 emission rates in the six illustrative scenarios in

the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-20). By 2100, HCFC-23 mixing ratios are about 32-34 ppt (35 ppt in 2050) in all IPCC scenarios.

1.7.6.3 HFC-125, HFC-143a, AND HFC-152a

The major use of HFCs -125 (CHF_2CF_3) and -143a (CH_3CF_3) is as refrigerants, whereas HFC-152a (CH_3CHF_2) is used primarily as a foam-blowing agent and aerosol propellant. The current tropospheric background abundance of these HFCs is relatively low, in the range of 1-3 ppt (Table 1-12; Prinn et al., 2000; Culbertson et al., 2000; Sturrock et al., 2001). Southern Hemispheric growth rates in mid-2000, based on measurements at Cape Grim, were about 0.2 ppt yr⁻¹ and 0.1 ppt yr⁻¹ for HFC-125 and HFC-152a, respectively (Sturrock et al., 2001).

IPCC (Prather and Ehhalt et al., 2001) calculated future HFC-125, -143a, and -152a abundances from 2000 to 2100 based on respective emission rates in the six illustrative scenarios in the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-20; HFC-143a not shown). By 2100, mixing ratios are about 60-140 ppt for HFC-125 (30-60 ppt in 2050), 90-200 ppt for HFC-143a (40-70 ppt in 2050), and 80 ppt for HFC-152a, (55 ppt in 2050) for all these IPCC scenarios.

1.7.7 Fluorocarbons (FCs), SF₆, and SF₅CF₃

Due to a combination of long atmospheric lifetimes (>1000 years) and strong infrared absorption cross sections, fluorocarbons (FCs) are among the most potent greenhouse gases known, having GWPs about 4 orders of magnitude higher than that of CO₂ (see Table 1-6). These gases are useful tracers of atmospheric transport in both the troposphere and the stratosphere. The only important sinks for FCs and sulfur hexafluoride (SF₆) are photolysis or ion reactions in the mesosphere.

1.7.7.1 CF₄ AND C₂F₆

The most abundant FCs in the present-day atmosphere are CF₄ (FC-14) and C₂F₆ (FC-116). Approximately 50% of the current atmospheric burden of CF₄ (~80 ppt) was present in preindustrial times, implying a natural, probably geochemical, source (Harnisch et al., 1996a; Harnisch and Eisenhauer, 1998). The predominant source of both compounds in recent times is believed to be the aluminum industry. Other minor sources include the semiconductor industry and from the production of CCIF₂CF₃ (CFC-115), where C₂F₆ can be formed as a byproduct due to overfluorination.

The current background atmospheric mixing ratio of CF₄ is about 80 ppt (Table 1-12; Harnisch et al., 1999;

Culbertson et al., 2000). The measurements of Harnisch et al. (1999) show that the growth rate of CF₄ has slowed in recent years from 1.07 ± 0.14 ppt yr⁻¹ over the period 1978-1990 to 0.72 ± 0.11 ppt yr⁻¹ between 1992 and 1998 (Figure 1-21). These growth rates correspond to global emission rates of (16.3 ± 2.0) × 10⁶ kg yr⁻¹ and (11.0 ± 1.7) × 10⁶ kg yr⁻¹ and, allowing for estimated emissions of CF₄ from the semiconductor industry, imply a reduction of CF₄ emissions from aluminum production of about 40%. This observation concurs with an aluminum industry estimate of a 30% decrease in FC emissions between 1990 and 1993 (Marks, 2000).

The current background atmospheric concentration of C₂F₆ is about 3 ppt (Harnisch et al., 1996b; Oram, 1999; Culbertson et al., 2000). Analysis of the Cape Grim air archive shows that the mixing ratio of C₂F₆ in the Southern Hemisphere has increased from 0.7 ppt in 1978 to 2.2 ppt in late 1995 (Figure 1-21; Oram, 1999). The growth rate over this period was approximately constant at 0.08 ppt yr⁻¹, which contrasts strongly with the behavior of CF₄ whose growth rate has declined since the early 1990s. Assuming emissions of C₂F₆ from aluminum production have fallen along with those of CF₄, an additional, increasing source of C₂F₆ is required to maintain a constant emission rate.

IPCC (Prather and Ehhalt et al., 2001) calculated future CF₄ and C₂F₆ abundances from 2000 to 2100 based on respective emission rates in the six illustrative scenarios in the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-21). Mixing ratios projected for 2100 in the range of IPCC scenarios are 210-400 ppt for CF₄ (135-185 ppt in 2050) and 10-25 ppt for C₂F₆ (7-10 ppt in 2050).

1.7.7.2 c-C₄F₈ AND C₃F₈

Since the previous Assessment (WMO, 1999), two other FCs have been detected in the background atmosphere, perfluorocyclobutane (c-C₄F₈; FC-318) and perfluoropropane (C₃F₈; FC-218). The origin of c-C₄F₈ is uncertain, although it is used in small amounts by the semiconductor industry (cleaning and plasma etching), and in very small amounts in some refrigeration blends (Harnisch, 2000). C₃F₈ is used for plasma etching and a small amount (~0.1 × 10⁶ kg yr⁻¹) is emitted during aluminum production (Harnisch, 1997, 2000).

The abundance of c-C₄F₈ at Cape Grim increased from 0.6 ppt in 1978 to about 1 ppt by late 1995 (Table 1-12; Figure 1-21; Oram, 1999). The 1995 growth rate of 0.012 ppt yr⁻¹ was about 80% lower than the maximum of 0.057 ppt yr⁻¹ measured over the period 1983-1989. In this way, its behavior is similar to that of CF₄, whose growth rate has slowed in response to reduced emissions

SOURCE GASES

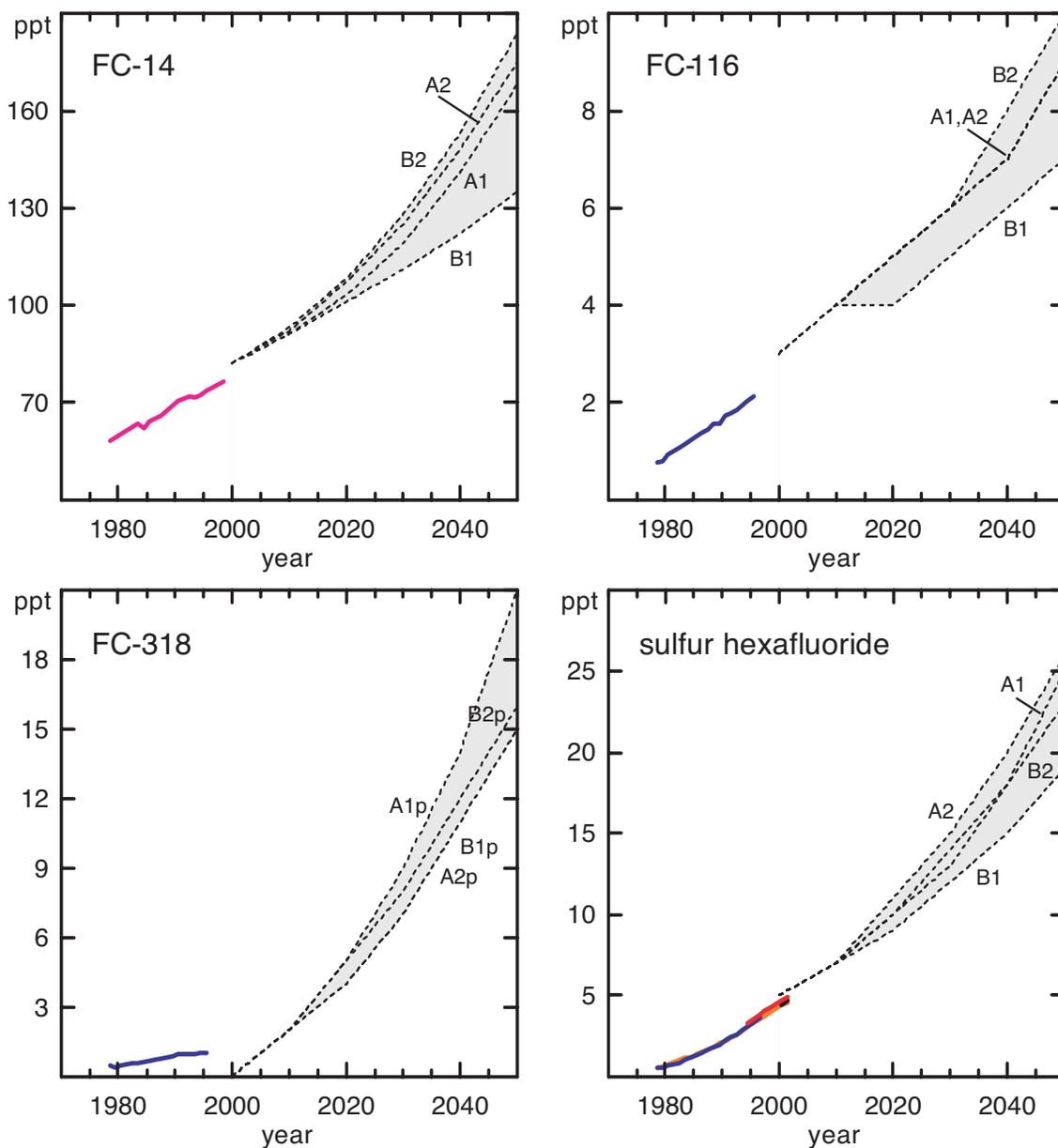


Figure 1-21. Long-term trends (annual mean data) and possible future levels of fluorocarbons and sulfur hexafluoride. Data are from the Northern Hemisphere (pink line: MPAE, Harnisch et al., 1999, FC-14 only), means from Cape Grim, Tasmania (blue lines: UEA, Oram, 1999; black line: SIO, Vollmer and Weiss, 2002, SF₆ only; orange line: UH, Maiss and Brenninkmeijer, 1998, SF₆ only), and global surface means (red line: CMDL, Hall et al., 2002, SF₆ only). The scenarios (plotted from 2000) are from IPCC (2001; Appendix II).

from the aluminum industry. However, *c*-C₄F₈ has not been reported in studies of the composition of emissions from aluminum plants, so the cause of the observed decrease in growth rate remains unclear. Measurements of *c*-C₄F₈ have also been reported in stratospheric air. Sturges et al. (2000a) reported a Northern Hemispheric, upper tropospheric mixing ratio of about 1.0 ppt for 1994,

and Travnicek (1998) reported a 1997 mixing ratio of 0.7 ppt and calculated an annual global emissions rate of about 0.7×10^6 kg yr⁻¹ over the period 1978-1997.

In recent years the first atmospheric measurements of C₃F₈ have also been reported. From a stratospheric profile collected in 1997, Sturges et al. (2000a) estimated an upper tropospheric mixing ratio of approximately 0.3

ppt. The full profile between 11 and 32 km implies a long atmospheric lifetime for this gas and recent tropospheric increases. In addition, Culbertson et al. (2000) measured a similar mean C_3F_8 mixing ratio of 0.26 ± 0.03 ppt in samples collected at a rural, continental U.S. site in March-April 2000.

1.7.7.3 SULFUR HEXAFLUORIDE (SF_6)

Sulfur hexafluoride (SF_6) is used mostly as an insulating fluid in step-down transformers and as a cover gas in magnesium production. Atmospheric SF_6 continues to rise (Table 1-12, Figure 1-21), with current (2000) global surface means estimated at 4.7 ppt (Hall et al., 2002) and global growth rates of 4-5% yr^{-1} . Vertical column abundances of SF_6 monitored above the Jungfrauoch increased by an average of 3.49×10^{12} molec $cm^{-2} yr^{-1}$ from 1987 to 2001, which corresponds to 12.9% yr^{-1} during 1987-1988 and 5.1% yr^{-1} during 1999-2000 (Zander et al., 2002). IPCC (Prather and Ehhalt et al., 2001) calculated future SF_6 abundances from 2000 to 2100 based on respective emission rates in the six illustrative scenarios in the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-21). By 2100 mixing ratios are estimated to be about 55-65 ppt (20-25 ppt in 2050) in all these scenarios.

1.7.7.4 TRIFLUOROMETHYLSULFURPENTAFLUORIDE (SF_5CF_3)

Another long-lived greenhouse gas has recently been found in the atmosphere (Sturges et al., 2000b). Trifluoromethylsulfurpentafluoride (SF_5CF_3) has an atmospheric lifetime of about 800 years (Table 1-3; Takahashi et al., 2002) and, on a per-molecule basis, has the largest radiative forcing of any gas found in the atmosphere to date. Measurements of SF_5CF_3 in air trapped in polar snow (firn) show its abundance has risen from near zero in the 1960s to about 0.12 ppt in 1999, and is currently growing at 0.008 ppt yr^{-1} . The only known source of SF_5CF_3 is as a byproduct of the manufacture of certain fluorinated chemicals (Santoro, 2000).

1.8 HALOGENATED SOURCE GASES IN THE FUTURE

Scenarios were developed to describe the range of future mixing ratios of ODSs given our current understanding of sources, sinks, banks or reservoirs of unemitted material and emission rates from these, and potential future production. The baseline scenario Ab was designed as a best estimate of future trace gas mixing ratios based upon current trends in production and con-

sumption, and limits to these as defined by the fully amended and adjusted Montreal Protocol. Scenario Am was an attempt to define atmospheric mixing ratios in a world where future production and consumption rates were at the maximum allowed by the fully amended and adjusted Montreal Protocol. It must be kept in mind that for some gases, notably the HCFCs, this concept is ill defined because upper limits to global production apply only after 2016. The Pc scenario was constructed to show how continued constant production of ODSs at 1999 rates into the future, in clear violation of the Montreal Protocol, would affect future EESC. Hypothetical scenarios were also developed in which emissions of all ODSs (E0) or a selected class of ODSs ceased in 2003. These hypothetical cases were constructed to show how future emissions of different compound classes affect future EESC and to define a lower limit to future EESC. Additional, potentially achievable cases were also constructed to show the effects of zero production from 2003 onward for groups of ODSs and all ODSs together (P0). More details regarding the assumptions made in developing these scenarios and cases are included in Tables 1-13 and 1-14.

1.8.1 Development of the Baseline Scenario Ab

To create the baseline scenario Ab, a set of emissions was derived for each halocarbon for 1950-2000 so that mixing ratios calculated in a simple box model would match as closely as possible the observed mixing ratios (Tables 1-15 and 1-16; Figure 1-22). Where possible, emissions were based on historical industry production data and emission functions as described in Section 1.3 (e.g., McCulloch and Midgley, 2001; McCulloch et al., 2001; AFEAS, 2001; UNEP, 2002). Some discrepancies exist, however, between measured and calculated mixing ratios (see Section 1.6), and in order to provide a history without discontinuities, scale factors were sometimes applied to these emissions to better match the observed atmospheric mole fractions (Tables 1-15 and 1-16).

Future emissions were derived for 2000-2100 based upon (1) current trends in halocarbon production and emission, (2) the size of unemitted reserves (adjusted to reflect scale factors applied to past emissions), (3) relationships between production and emission as a function of application, and between reserves and emission, and (4) considering future production restrictions outlined in the latest Amendments (Beijing) of the Montreal Protocol. The Beijing Amendments (1999) to the Montreal Protocol included limits on the production of HCFCs in both developed (freeze in 2004) and developing (freeze in 2016) countries, stricter limits on the production of ODSs by

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developed countries for use in developing countries, as well as a global phaseout of a new species, bromochloromethane (CH_2BrCl), in 2002.

For methyl chloride and methyl bromide, scenarios were developed for past years based upon available firm air and real-time measurements (Khalil et al., 1993; Khalil and Rasmussen, 1999; Butler et al., 1999; Sturges et al., 2001a). Mixing ratios were set for the late 1990s at 9.5 ppt CH_3Br and 550 ppt for CH_3Cl based upon discussions in Kurylo and Rodríguez et al. (1999). Future mixing ratios in scenarios were calculated assuming that restrictions on production resulted in emission reductions in the same year (Table 1-13). Future emissions of CH_3Cl were kept constant to sustain a mixing ratio of 550 ppt for all scenarios.

1.8.2 Projecting Future Halocarbon Mixing Ratios

Future mixing ratios of a trace gas depend upon future emission rates and the rate at which the gas is removed from the atmosphere. Atmospheric removal rates are determined by the chemical and physical characteristics of a trace gas, and cannot be purposefully altered by humans. In the absence of emissions, future mixing ratios can be calculated on the basis of trace gas lifetimes. Because lifetimes of ODSs range from less than 1 year to more than 100 years, however, the expected rate of decline in the absence of emissions varies substantially for different halocarbons.

Emissions of most ODSs, however, are not yet insignificant. Substantial amounts of some ODSs exist in current applications and will be released to the atmosphere in future years. Furthermore, production of some halocarbons continues under the allowances prescribed by the Montreal Protocol. Predicting future mixing ratios of ODSs requires a good understanding of emission rates of ODSs from present-day applications, the size of produced but unemitted reserves (banks), the magnitude of future production, and halocarbon atmospheric lifetimes. Managing or controlling future mixing ratios is possible only through controlling current rates of emission and future production.

In what follows, some salient points regarding future halocarbon mixing ratios and the development of scenarios are discussed.

1.8.2.1 CFCs

Reserves of unemitted but produced CFCs vary substantially for different individual CFCs because they were used in different applications. CFC-11 was used extensively in foams from which only a small portion of the CFC becomes released each year. As a result a very

large reservoir of CFC-11 exists in foams today, and future emissions will depend mostly upon the rate at which CFC-11 escapes from foams together with the amount of future production. Emission models suggest that the reservoir of unemitted CFC-12 and -113 is substantially smaller, owing to use in applications where release is more rapid (AFEAS, 2001). For these two gases, future emissions will be more closely tied to the magnitude of future production. Differences in the calculated future scenarios reflect the size of reserves for each gas relative to the potential magnitude of future production (Figure 1-1).

1.8.2.2 METHYL CHLOROFORM

Reserves of produced but unemitted methyl chloroform (CH_3CCl_3) are thought to be small owing to past use predominantly as a solvent and cleaning agent. Accordingly, future emissions should be closely tied to future production. Known production in recent years has been about 20 Gg yr^{-1} (McCulloch and Midgley, 2001), or quite small compared with earlier years, and should decrease as the allowances for production and consumption in developing countries diminish through 2015. The exponential decline in mixing ratios in recent years will continue as long as methyl chloroform emissions remain small relative to its atmospheric burden. Future production within limits allowed by the Protocol could slow this decline (Figure 1-4). Furthermore, if some nonindustrial emissions exist and persist in the future, perhaps as a result of biomass burning (Rudolph et al., 2000), the exponential rate of decay would slow until some non-zero steady-state mixing ratio was reached. Current estimates of non-industrial emission magnitudes suggest that this steady-state mixing ratio would be <2 ppt (see Section 1.3).

1.8.2.3 CARBON TETRACHLORIDE

Significant mismatches between observed and calculated mixing ratios of carbon tetrachloride (CCl_4) suggest potential difficulty in reliably estimating future amounts of this important ODS (see Section 1.6). Improvements in this area will come only after certain questions are addressed. These questions include the following: (1) How much carbon tetrachloride is emitted from processes not related to the production of CFCs, and how have these releases changed over time? (2) Are fugitive releases of CCl_4 on the order of 11% from production of CFCs in the years 1978-1993 reasonable? (3) Did those fugitive releases more than double to become about 25% in 1995-1999 as the bulk of CFC production shifted to countries operating under Article 5(1) of the Montreal Protocol (Figure 1-15; Article 5(1) refers to developing countries as defined by the Montreal Protocol)?

Table 1-13. Description of scenarios for future ODS emissions.

Scenario	Description
Ab: Baseline (best-guess scenario following the Beijing Amendments, 1999) = Reference	<p>Developed countries (non-Article 5(1)): Future production of CFCs was continued at the current level of capacity for "essential uses" and export to Article 5(1) countries. The bank of unemitted reserves in 2000 was estimated to be 656 Gg for CFC-11 and 60 Gg for CFC-12. Future production of CCl₄ was governed by the quantities required for CFC manufacture; global emissions of CCl₄ were estimated as a fraction (40%) of global CFC production (see Figure 1-15). Future production of methyl chloroform was zero. Emission of halons in future years was estimated as a percentage of unemitted global reserves: 98 Gg for Halon-1211 and 62 Gg for Halon-1301 in 2000. Production of HCFCs was continued with the same trends as now; after 2003 production is assumed to decline according to consumption limits required by the Protocol. Controls on global production of CH₃Br were presumed to result in a global emission decrease of 30 Gg yr⁻¹ (out of 212 Gg yr⁻¹) in the future as governed by the phase-out schedule of the Protocol; 75% of this emission was phased out according to the schedule for production decreases in non-Article 5(1) countries, and 25% was phased out according to this schedule in Article 5(1) countries. Emissions from quarantine pre-shipment applications were held constant into the future at 12 Gg yr⁻¹; emissions from biomass burning and gasoline combustion were also held constant in all scenarios.</p> <p>Developing countries (Article 5(1)): Production of CFCs and methyl chloroform was allowed to continue at the current (frozen) level, with phase down dates mandated in the Montreal Protocol, and there was no production allotted in Countries with Economies in Transition (the de facto situation). Emissions of carbon tetrachloride were estimated at almost 40% of CFC-11 and -12 produced. Emissions of halons were estimated as a percentage of unemitted global reserves. The size of this unemitted stock of Halon-1211 in 2000 was enhanced slightly to account for potential additional production in Article 5(1) countries. For Halon-1301 production in A5(1) countries was taken from Fraser et al. (1999). Production and consumption of HCFCs was kept constant at current levels until phase down is required (after 2015). For a discussion of future production and emission of CCl₄ and CH₃Br, see the discussion for non-Article 5(1) countries.</p>
Am: Maximum production	<p>Production of CFCs, halons, and HCFCs is projected forward at the maximum allowed under the Protocol.</p> <p>CFCs: The maximum global production allotment for CFCs is, according to UNEP (2002), 160 ODP-ktons yr⁻¹ through 2004, decreasing to zero in 2010. This is 17.5% above the 1999 production in the Ab scenario. For the maximum scenario, the Ab production of CFC-11, -12, and -113 was therefore multiplied by 1.175 for the years 2000-2004 (a scale factor of 1.0 was applied to CFC production during 2005-2009). The emissions of carbon tetrachloride were consequently also multiplied by the same factor, since they are linked in the calculation to the production of CFC-11 and -12. The UNEP production limit for CCl₄ was not applied.</p> <p>Halons: For Halon-1211 a global bank of 114 Gg in 2000 was used, instead of 98 Gg as in Ab. For the combined halons, a total global production was applied of 45 ODP-ktons through 2004, and 22.5 ODP-ktons split among the years 2005-2009. This production was divided over Halon-1211 and -1301 according to their production split in 1999 in the Ab scenario.</p> <p>HCFCs: Future production and consumption of HCFCs was estimated by keeping production in non-Article 5(1) countries constant at the 1999 level of 27 ODP-ktons yr⁻¹ and by increasing production in Article 5(1) countries by 3% yr⁻¹ starting in 1999 at 9.4 ODP-ktons yr⁻¹. The Protocol limits for production and consumption were applied for later years. The production of HCFCs in future years was split among HCFC-22, -141b, and -142b, as it was in 1999 (AFEAS, 2001). Production of methyl chloroform and methyl bromide are all at their practical maxima and so are the same as in the Ab scenario.</p>
Pc: Continued production	<p>Continued production of all ODSs at a constant level reported by UNEP (2002) for the year 1999 was assumed. This additional production would be in excess of the limits set by the amended Montreal Protocol. Global production magnitudes reported by UNEP (ODP-Gg yr⁻¹) for 1999 and used in this scenario were: 147.2 for CFCs, 25.2 for halons, 1.78 for methyl chloroform, and 36.2 for HCFCs. Carbon tetrachloride production was kept constant in the future at 67.7 Gg yr⁻¹ based upon production of CFC-11 and -12 in 1999. Methyl bromide emission was held constant at the 1999 level. For the CFCs (CFC-11, -12, and -113), halons (1211 and 1301), and HCFCs (HCFC-22, -141b, and -142b), the 1999 production of the individual species was calculated from the aggregated ODP-weighted UNEP total using the ratio in the Ab scenario for 1999.</p>

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Table 1-14. Description of cases for future ODS production and emissions.

Case	Description
E0: Zero emission (hypothetical scenario)	Anthropogenic emissions of all ODSs set to zero from 2003 onward, i.e., banks destroyed and production stopped. In practice, this is an unachievable scenario. This case is used to show the natural removal rates of ODS from the atmosphere and describes a lower limit for ODS mixing ratios in the future atmosphere.
Emission contribution of CFCs to Ab	No emission of CFCs (including from existing equipment) from 2003 onward. Other species as in scenario Ab.
Emission contribution of CCl ₄ to Ab	No emission of carbon tetrachloride (including from existing equipment) from 2003 onward. Other species as in scenario Ab. Since the emissions of CCl ₄ are fugitive and in the calculations related to the production of CFC-11 and -12, this is the same as a zero production case.
Emission contribution of CH ₃ CCl ₃ to Ab	No emission of methyl chloroform (including from existing equipment) from 2003 onward. Other species as in scenario Ab.
Emission contribution of halons to Ab	No emission of halons (including from existing equipment) from 2003 onward. Other species as in scenario Ab.
Emission contribution of HCFCs to Ab	No emission of HCFCs (including from existing equipment) from 2003 onward. Other species as in scenario Ab.
Emission contribution of CH ₃ Br to Ab	No anthropogenic emission of methyl bromide (including from existing equipment) from 2003 onward. Total reduction of 42 Gg (30 for controllable uses and 12 for Quarantine and Pre-Shipment (QPS) uses). Other species as in scenario Ab. The emissions of CH ₃ Br are from dispersive uses, so there is no substantial bank. As a result, this case is identical to a zero methyl bromide production case. Nonindustrial emissions of 160-170 Gg yr ⁻¹ were presumed and were kept constant in the future.
P0: Zero production	Production of all ODSs set to zero from 2003 onward. Emissions continue based upon size of unemitted reserves (based on the cases described below).
Production contribution of CFCs to Ab	No production of CFCs from 2003 onward. Emission of CFC-12 equals its production after 2002 (bank is depleting rapidly), so for CFC-12 this equals zero emissions. Production of CFC-114 and -115 already zero in Ab. Non-CFCs as in scenario Ab.
Production contribution of CH ₃ CCl ₃ to Ab	No production of methyl chloroform from 2003 onward. Other species as in scenario Ab.
Production contribution of halons to Ab	No production of halons from 2003 onward. Global production of Halon-1211 and -1301 in 1999 is, according to Fraser et al. (1999), 29.0 ODP-ktons and according to UNEP (2002), 25.2 ODP-ktons in 1999. This case was derived by estimating emissions from the halon production predicted in Fraser et al. (1999) for 2003-2009 (zero after 2009) and subtracting these emissions from those calculated in the Ab scenario. Halon-1202 emissions were presumed to be zero, since they arise as a byproduct of Halon-1211 production. Halon-2402 production was limited to Russia. The amount produced decreased rapidly from 2.45 ktons in 1990 to 0.152 ktons in 1999 (UNEP, 1999). The 1996 number is only a small fraction of the emission. Halon-2402 production is therefore assumed zero in this case (from 2003 onward) (same as in Ab, in agreement with Madronich and Velders et al. (1999) and Fraser et al. (1999)).
Production contribution of HCFCs to Ab	No production of HCFCs from 2003 onward. Other gases as in scenario Ab.
Production contribution of CH ₃ Br to Ab	No production of CH ₃ Br from 2003 onward. Because emissions are presumed to be prompt after production, this case is identical to the case of zero CH ₃ Br emissions.

Table 1-15. Source of production, emission, and observation data used in creating scenarios.

	Details Related to Creating Mean Set of Global Observations ^a			Details Related to Calculating Expected Mixing Ratios and Past Mixing Ratios in Scenarios from a Simple Box Model Calculation ^b			
	Mean AGAGE/CMDL Ratio (s.d.)	Period of Overlap	Source of Mean Observations after Scaling ^c	Lifetime Used In Box Model (years)	Production Data Source	Emission Function Revised?	Emission Scale Factor ^d
CFC-12	1.008 (0.002)	1991-1999	AGAGE	100	AFEAS, UNEP	No	1.045 (1980) 0.8 (1993-94)
CFC-11	0.980 (0.002)	1990-1999	AGAGE	45	AFEAS, UNEP	Yes, foam ^e	1.068
CFC-113	0.993 (0.005)	1994-1999	AGAGE	85	AFEAS only	No	0.98
CCl ₄	0.973 (0.006)	1993-1999	AGAGE	26	f	f	f
CH ₃ CCl ₃	0.975 (0.008)	1993-1999	AGAGE	4.8	g	No	Variable (0.9 to 1.25)
HCFC-22	0.993 (0.007)	1998-2000	CMDL	11.8	AFEAS, UNEP	No	1.0
HCFC-141b	1.011 (0.006)	1998-2000	CMDL	9.2	AFEAS, UNEP	No	1.0
HCFC-142b	1.049 (0.008)	1998-2000	CMDL	18.5	AFEAS, UNEP	Yes, foam ^h	1.0
Halon-1211	1.068 (0.006)	1998-2000	CMDL	16	i	No	1.18 (1992)
Halon-1301	1.139 (0.004)	1998-2000	CMDL	65	j	No	Variable
CH ₃ Br	NA	NA	k	0.7	NA	NA	NA
CH ₃ Cl	NA	NA	l	1.3	NA	NA	NA

NA, Not available.

^a Mean halocarbon measurements were derived from the longest available global data record after adjusting this data record by the factor $[1 \pm (1-x)/2]$, where x is the mean AGAGE/CMDL ratio indicated. Scenarios were created to match these measurements for past years. AGAGE data are reported on the SIO-98 scale (Prinn et al., 2000); CMDL data are reported on scales as described in Hall et al. (2002).

^b Calculated mixing ratios also appear in Scenarios and provide the basis for calculating future emissions and mixing ratios. Citations referred to are AFEAS (2001) and UNEP (2002) unless otherwise specified.

^c Data record from the group indicated was scaled by half the AGAGE vs. CMDL ratio.

^d To create a set of emissions consistent with global observations (Section 1.8 only), emissions derived from industrial production were scaled by this factor up to the point at which measurements become available.

^e McCulloch et al. (2001).

^f CCl₄ emission estimated in the future from CFC-11 and -12 production (see text).

^g McCulloch and Midgley (2001).

^h Emission functions for foams adjusted as described in Ashford (2000) and McCulloch et al. (2001).

ⁱ Updated UNEP (1999).

^j Fraser et al. (1999).

^k Southern Hemispheric firm data were scaled by a constant of 1.16 to approximate global mixing ratios (see Section 1.5).

^l Southern Hemispheric firm data were scaled by a constant of 1.06 to approximate global mixing ratios (see Section 1.5).

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Table 1-16. Calculated global surface mixing ratios (ppt) in the Ab baseline scenario. Dates are for the beginning of the year indicated.

Year	CFC-12		CFC-114			CCl ₄	HCFC-22		HCFC-142b		Halon-1202		Halon-2402		CH ₃ Cl	
	CFC-11	CFC-113	CFC-115			CH ₃ CCl ₃	HCFC-141b	Halon-1211	Halon-1301	CH ₃ Br						
1990	256.3	474.1	68.0	15.4	5.1	105.7	124.7	82.0	0.0	1.2	2.27	0.03	1.66	0.31	9.0	550.5
1991	262.6	488.0	74.0	15.7	5.6	105.8	128.8	88.1	0.0	1.7	2.54	0.03	1.85	0.34	9.0	550.6
1992	267.4	500.2	78.3	15.9	6.0	105.5	129.1	94.4	0.0	2.4	2.79	0.03	1.98	0.36	9.1	550.6
1993	271.2	511.5	81.4	16.0	6.5	105.1	127.8	100.8	0.2	3.3	2.94	0.03	2.07	0.38	9.2	550.6
1994	271.2	518.7	82.9	16.1	7.0	104.5	118.8	106.8	0.9	4.2	3.10	0.04	2.17	0.40	9.3	550.7
1995	270.6	524.8	83.2	16.2	7.5	103.7	107.8	112.8	2.1	5.2	3.25	0.04	2.33	0.42	9.4	550.7
1996	269.5	530.0	83.2	16.2	7.9	102.7	97.0	118.6	3.8	6.3	3.40	0.04	2.46	0.43	9.5	550.7
1997	268.2	534.2	82.7	16.3	8.3	101.6	82.9	125.0	5.5	7.4	3.55	0.05	2.55	0.43	9.5	550.7
1998	266.6	537.4	82.6	16.3	8.6	100.5	69.3	130.5	7.1	8.5	3.69	0.05	2.64	0.43	9.5	550.7
1999	264.7	539.5	82.3	16.3	8.8	99.2	58.6	136.1	9.0	9.4	3.83	0.05	2.73	0.42	9.5	550.7
2000	262.6	540.5	81.7	16.4	9.0	97.9	49.9	141.6	10.8	10.5	3.97	0.05	2.82	0.41	9.3	550.7
2001	260.5	541.2	81.1	16.4	9.1	96.7	42.6	149.3	13.0	12.2	4.07	0.04	2.90	0.41	9.3	550.7
2002	258.2	541.9	80.4	16.4	9.1	95.5	36.6	156.4	15.4	13.9	4.13	0.04	2.97	0.40	9.1	550.7
2003	255.8	542.7	79.6	16.4	9.1	94.4	31.6	162.9	18.1	15.5	4.16	0.03	3.04	0.39	9.0	550.7
2004	253.3	541.9	78.8	16.4	9.2	93.3	27.5	168.9	20.9	17.1	4.16	0.03	3.11	0.38	8.9	550.7
2005	250.7	541.1	78.0	16.4	9.2	92.3	24.0	174.4	23.8	18.7	4.14	0.02	3.17	0.37	8.8	550.7
2006	248.0	538.5	77.2	16.4	9.2	90.3	21.2	178.2	26.5	20.1	4.09	0.02	3.23	0.36	8.5	550.7
2007	245.2	536.0	76.3	16.4	9.2	88.5	18.8	180.6	28.9	21.3	4.03	0.02	3.28	0.35	8.5	550.7
2008	242.4	531.4	75.5	16.3	9.2	85.6	16.7	182.0	31.1	22.3	3.95	0.01	3.32	0.34	8.4	550.7
2009	239.3	526.9	74.7	16.3	9.2	82.8	15.0	182.7	33.0	23.2	3.86	0.01	3.37	0.32	8.4	550.7
2010	236.1	522.5	73.9	16.3	9.2	80.1	13.6	182.8	34.8	24.0	3.76	0.01	3.40	0.31	8.4	550.7
2011	232.7	517.3	73.0	16.2	9.2	77.1	12.3	182.5	36.5	24.7	3.66	0.01	3.44	0.30	8.4	550.7
2012	229.2	512.2	72.2	16.2	9.2	74.2	11.2	180.8	37.7	25.2	3.54	0.00	3.46	0.29	8.4	550.7
2013	225.6	507.1	71.3	16.2	9.2	71.4	10.3	178.2	38.5	25.5	3.43	0.00	3.49	0.28	8.4	550.7
2014	221.9	502.0	70.5	16.1	9.2	68.7	9.5	174.8	39.1	25.6	3.31	0.00	3.51	0.27	8.4	550.7
2015	218.2	497.0	69.7	16.1	9.2	66.1	8.7	171.0	39.4	25.7	3.19	0.00	3.52	0.26	8.4	550.7
2016	214.3	492.1	68.9	16.0	9.1	63.6	8.0	167.0	39.6	25.7	3.07	0.00	3.54	0.25	8.2	550.7
2017	210.5	487.2	68.1	16.0	9.1	61.2	7.4	162.0	39.3	25.5	2.95	0.00	3.55	0.24	8.2	550.7
2018	206.6	482.3	67.3	15.9	9.1	58.9	6.9	156.2	38.8	25.1	2.83	0.00	3.55	0.23	8.2	550.7
2019	202.7	477.5	66.5	15.9	9.1	56.7	6.3	150.1	38.0	24.7	2.71	0.00	3.56	0.22	8.2	550.7
2020	198.9	472.8	65.7	15.8	9.1	54.6	5.9	143.9	37.1	24.1	2.59	0.00	3.56	0.21	8.2	550.7
2021	195.0	468.1	64.9	15.8	9.1	52.5	5.4	137.6	36.1	23.6	2.48	0.00	3.55	0.20	8.2	550.7
2022	191.2	463.4	64.2	15.7	9.1	50.5	5.0	131.2	34.9	22.9	2.37	0.00	3.55	0.19	8.2	550.7
2023	187.4	458.8	63.4	15.7	9.1	48.6	4.7	124.8	33.7	22.3	2.26	0.00	3.54	0.18	8.2	550.7
2024	183.6	454.2	62.7	15.6	9.1	46.8	4.3	118.6	32.4	21.6	2.16	0.00	3.53	0.18	8.2	550.7
2025	179.9	449.7	62.0	15.6	9.1	45.0	4.0	112.6	31.0	20.9	2.05	0.00	3.52	0.17	8.2	550.7
2030	162.0	427.8	58.4	15.3	9.1	37.1	2.8	86.8	24.7	17.6	1.59	0.00	3.44	0.13	8.2	550.7
2035	145.5	406.9	55.1	15.1	9.0	30.6	1.9	66.9	19.1	14.6	1.22	0.00	3.33	0.10	8.2	550.7
2040	130.5	387.1	51.9	14.8	9.0	25.3	1.3	51.6	14.6	12.0	0.93	0.00	3.19	0.08	8.2	550.7
2045	116.9	368.2	49.0	14.6	9.0	20.9	0.9	39.3	11.0	9.8	0.70	0.00	3.04	0.06	8.2	550.7
2050	104.7	350.2	46.2	14.4	9.0	17.2	0.6	27.6	7.7	7.6	0.52	0.00	2.88	0.05	8.2	550.7
2055	93.8	333.2	43.5	14.1	8.9	14.2	0.5	18.7	5.2	5.8	0.39	0.00	2.72	0.04	8.2	550.7
2060	83.9	316.9	41.0	13.9	8.9	11.7	0.3	12.5	3.4	4.4	0.29	0.00	2.56	0.03	8.2	550.7
2065	75.1	301.5	38.7	13.7	8.9	9.7	0.2	8.3	2.1	3.4	0.21	0.00	2.41	0.02	8.2	550.7
2070	67.2	286.8	36.5	13.4	8.9	8.0	0.2	5.5	1.3	2.6	0.16	0.00	2.25	0.02	8.2	550.7
2075	60.2	272.8	34.4	13.2	8.8	6.6	0.1	3.6	0.8	1.9	0.12	0.00	2.11	0.01	8.2	550.7
2080	53.8	259.5	32.4	13.0	8.8	5.4	0.1	2.4	0.5	1.5	0.09	0.00	1.97	0.01	8.2	550.7
2085	48.2	246.8	30.6	12.8	8.8	4.5	0.1	1.6	0.3	1.1	0.06	0.00	1.83	0.01	8.2	550.7
2090	43.1	234.8	28.8	12.6	8.8	3.7	0.0	1.0	0.2	0.8	0.05	0.00	1.71	0.01	8.2	550.7
2095	38.6	223.3	27.2	12.4	8.7	3.1	0.0	0.7	0.1	0.6	0.03	0.00	1.59	0.01	8.2	550.7
2100	34.5	212.4	25.6	12.2	8.7	2.5	0.0	0.5	0.1	0.5	0.03	0.00	1.48	0.00	8.2	550.7

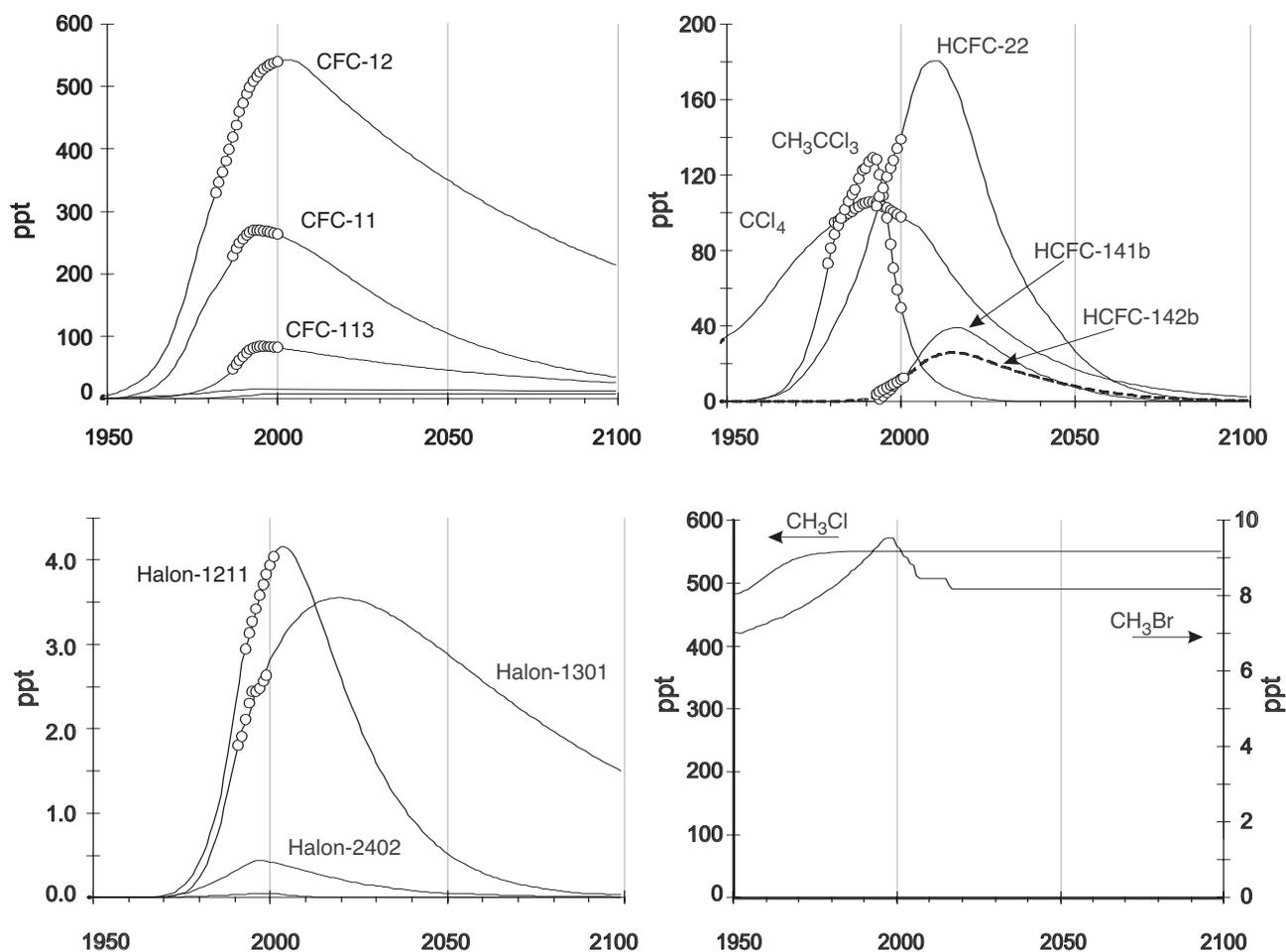


Figure 1-22. Global atmospheric surface mixing ratios (ppt) in the baseline scenario Ab (lines) and the mean AGAGE-CMDL observations (circles; see Table 1-15 for origin; Prinn et al., 2000; Montzka et al., 1999).

In the Ab and Am scenarios, future emissions of CCl₄ were estimated from CFC production and a molar ratio [*total* CCl₄ emission]/[global CFC production] of 0.38 as estimated for recent years (see Figure 1-15). These projections (Figure 1-4) will be reasonable for carbon tetrachloride only if *all* significant emissions of this gas become diminished in the future along the time frame projected for reductions in CFC production.

1.8.2.4 HALONS

A large fraction of present-day halon emissions arise from use of a banked halon, defined here as material that is contained in inventories and installed equipment. As a result, future mixing ratios are tied to the rate of emissions from these halon banks in addition to the magnitude of future production (Figure 1-3). Although progress has been made in reducing production for future uses (UNEP, 1997), halon banks are large relative to current emission

rates (Butler et al., 1999; Fraser et al., 1999; UNEP, 1999, and updates). In the Ab scenario, mixing ratios of Halon-1301 continue to increase until about 2020 primarily because of emission from reserves. Scenario results for Halon-1211 also suggest that emissions from reserves are important, but the magnitude and date of peak mixing ratios are strongly influenced by future production rates as well (Figure 1-3).

Additional uncertainty in future halon mixing ratios arises because the size of these reserves is not well defined; this added uncertainty is not explicitly included in the calculated scenarios but is considered elsewhere (see Section 1.8.4). For Halon-1211, estimates of reserves derived from production data and functions relating releases to production vary from 65 to 136 Gg in 2000 (Fraser et al., 1999; UNEP, 1999, updated). Reserves calculated with emissions derived from atmospheric measurements (Butler et al., 1998, 1999) and an atmospheric lifetime of 16 years are about 100 Gg in 2000; those

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derived from independent measurements at Cape Grim by UEA (Fraser et al., 1999) are substantially smaller. For reference, current increases observed for Halon-1211 of 0.1 ppt yr^{-1} would require emissions of about 10 Gg yr^{-1} to sustain (for a 16-yr lifetime). For Halon-1301, estimates of reserves range from 45 Gg (UNEP, 1999, updated) to 65 Gg (Fraser et al., 1999) and, for reference, measurements suggest annual emissions of about 3 Gg yr^{-1} (for a 65-yr lifetime).

1.8.2.5 HCFCs

Uncertainty in future mixing ratios of HCFCs stems primarily from projecting how these gases will fulfill the needs of developing nations. Consumption is currently frozen in non-Article 5(1) countries, and soon reductions in consumption will be mandated there as well (see Figure 1-18). Production in non-Article 5(1) countries, however, is capped only after 2004; this production could provide a substantial allotment of HCFC for use in Article 5(1) countries, depending upon demand. In addition, production in Article 5(1) countries is not restricted until after 2015, although the extent to which these countries would invest substantial capital in the manufacture and use of such time-limited materials remains a major uncertainty. Production (as ODP-tons) in developing countries averaged 10% of production in non-Article 5(1) countries in the late 1990s (UNEP, 2002).

In the Ab scenario, future global HCFC production was presumed to decrease according to the consumption limits outlined for non-Article 5(1) countries and a small, constant allotment was included for production in countries operating under Article 5(1) of the Protocol. This scenario would underestimate future production, emissions, and consequent mixing ratios of HCFCs if demand for these gases in developing countries increased substantially in future years. In the Am scenario, production and consumption of HCFCs was increased as described in Table 1-13. This enhanced demand leads to higher HCFC mixing ratios in the future (Figure 1-5); this enhanced HCFC production accounts for about one-third of the 14.5% higher integrated EESC calculated for scenario Am compared with scenario Ab (Table 1-17).

1.8.2.6 METHYL BROMIDE AND METHYL CHLORIDE

Atmospheric releases resulting from industrial production represent only a fraction of total releases of these gases to today's atmosphere (see Section 1.5). Uncertainty in the magnitude of this fraction limits our ability to accurately describe how methyl bromide mixing ratios will respond to production limits in the revised and amended Montreal Protocol (Section 1.5.1.4). Scenarios

for methyl bromide were developed by prescribing future emission decreases of about 30 Gg , or 15% of the total annual flux, according to the schedule of production restrictions in the current Protocol (Table 1-13; see also Section 1.5). Anthropogenic emissions from quarantine and pre-shipment applications (12 Gg yr^{-1}) and from non-fumigation activity (biomass burning and automobile emissions) were kept constant in the future in all scenarios. No limits apply to methyl chloride production or consumption; total emissions of this gas were held constant in the future in all scenarios.

Both methyl bromide and methyl chloride are unique among ozone-depleting halocarbons because a substantial fraction of their sources and sinks arises from biological processes. These processes may be affected significantly by changes in future climate. Because our understanding of these processes is limited, we cannot predict if such changes would act to enhance or diminish mixing ratios of these gases in the future atmosphere (see also Section 1.8.5).

1.8.2.7 EFFECTIVE EQUIVALENT CHLORINE

As the influence of methyl chloroform on effective equivalent chlorine (EECI) has lessened, the decline observed for EECI has slowed (see Section 1.2; Figure 1-9). This is because mixing ratios of CFC-12, halons, and the HCFCs continued to increase in 2000. Future trace gas trends in scenario Ab (the best-guess scenario) result in continued declines in EECI in the near future; the mean rate of change for EECI during 2000-2010 in this scenario is $-0.9\% \text{ yr}^{-1}$ (Figure 1-9). In scenario Ab, EECI continues to decline because projected mixing ratios for CFC-12 and total bromine peak and subsequently begin decreasing during 2000-2005, and because enhanced declines in other CFCs are projected for that period as well (Figure 1-22). In scenario Am, EECI decreases at $-0.7\% \text{ yr}^{-1}$, slightly slower than in the Ab scenario.

1.8.3 Scenario Results: Calculated Mixing Ratios and EESC

The concept of effective equivalent stratospheric chlorine (EESC) has been used in the past to gauge the net effect of tropospheric halocarbon trends on the loading of ozone-depleting halogen in the stratosphere (Prather and Watson, 1990; Solomon and Wuebbles et al., 1995; Madronich and Velders et al., 1999; Daniel et al., 1995). As such, EESC provides a rough estimate of the time scale for ozone recovery in an otherwise unchanging atmosphere. The concept of EESC has limitations, however, particularly because of stratospheric mixing processes and other effects (Prather, 1997; see also discussion in Section

Table 1-17. Comparison of scenarios and cases: the year when EESC drops below the 1980 level, and integrated EESC differences (relative to baseline scenario Ab).^a

Scenarios and Cases	Year (x) when EESC is expected to drop below 1980 value ^a	Percent difference in $\int_{1980}^x \text{EESC } dt$ above the 1980 level relative to scenario Ab ^a	Percent difference in $\int_{2002}^x \text{EESC } dt$ above the 1980 level relative to scenario Ab ^a
Scenarios			
Ab: Beijing Amendments (1999)	2043.9	0.0	0.0
Am: Maximum allowed production	2048.0	8.3	14.5
Pc: Continued production	Not reached	>115 ^b	>202 ^b
Cases^c			
P0: Zero production of all anthropogenic ODSs	2039.9	-8.1	-14.1
Contribution CFC production to Ab	2042.8	-2.2	-3.8
Contribution CH ₃ CCl ₃ production to Ab	2043.9	-0.2	-0.3
Contribution Halon production to Ab	2043.6	-0.6	-1.1
Contribution HCFC production to Ab	2042.6	-3.1	-5.4
Contribution anthropogenic CH ₃ Br production to Ab	2042.9	-2.3	-4.0
E0: Zero emission of all anthropogenic ODSs	2033.8	-19.3	-33.8
Contribution CFC emissions to Ab	2041.1	-5.4	-9.4
Contribution CCl ₄ emissions to Ab	2043.5	-1.5	-2.7
Contribution CH ₃ CCl ₃ emissions to Ab	2043.7	-0.9	-1.6
Contribution Halon emissions to Ab	2040.7	-6.1	-10.8
Contribution HCFC emissions to Ab	2042.3	-4.9	-8.6
Contribution anthropogenic CH ₃ Br emissions to Ab	2042.9	-2.3	-4.0

^a The dates and percent differences in integrated EESC were calculated with the fractional release values in column 2 of Table 1-4.

^b The integrated percent differences indicated for Scenario Pc represent lower limits because the integration was run only through 2100 and EESC in this scenario does not reach the 1980 level by 2100 (see Figure 1-23).

^c Contributions of ozone-depleting substances to future EESC were calculated in the hypothetical "Cases" by setting production or emission to zero in 2003 and subsequent years for the indicated chemical or group of chemicals.

1.2.5). Furthermore, the chemical and dynamical state of the atmosphere has not been constant, and changes in aerosols, trace gas mixing ratios, and stratospheric temperatures are also expected to influence ozone chemistry and the efficiency of halogens to deplete stratospheric ozone in the future. Whereas different scenarios are gauged in this chapter in terms of integrated EESC and the date when EESC returns to the value estimated for 1980, discussions relating to future ozone concentrations in light of the broad range of additional atmospheric changes that are possible can be found in Chapters 3 and 4.

EESC was calculated as described in past Assessments for the updated scenarios. These calculations were performed with a slightly reduced efficiency for bromine relative to chlorine, on a per-atom basis, for the destruction of ozone compared to WMO (1999) ($\alpha = 45$; see Section 1.4.4). Furthermore, an absolute fractional

release of 0.8 for CFC-11 was included in this calculation to provide consistency with past reports, although the data of Schauffler et al. (2002) suggest that a more appropriate estimate may be 0.55. This absolute degradation amount does not affect calculations of ODP or relative changes in EESC presented in this chapter, but it is important when considering the influence short-lived gases have on the burden of ozone-depleting halogen, particularly in the lower stratosphere (see Chapter 2).

Despite the limitations of EESC, different scenarios and cases are compared with respect to the year (x) EESC returns to the value estimated for 1980, and by the percentage differences in time-integrated EESC from 2002 or 1980 through the year (x) (Table 1-17; Solomon and Wuebbles et al., 1995; Madronich and Velders et al., 1999). Because of the revised value for alpha, and because time-varying past histories for CH₃Br and CH₃Cl are now

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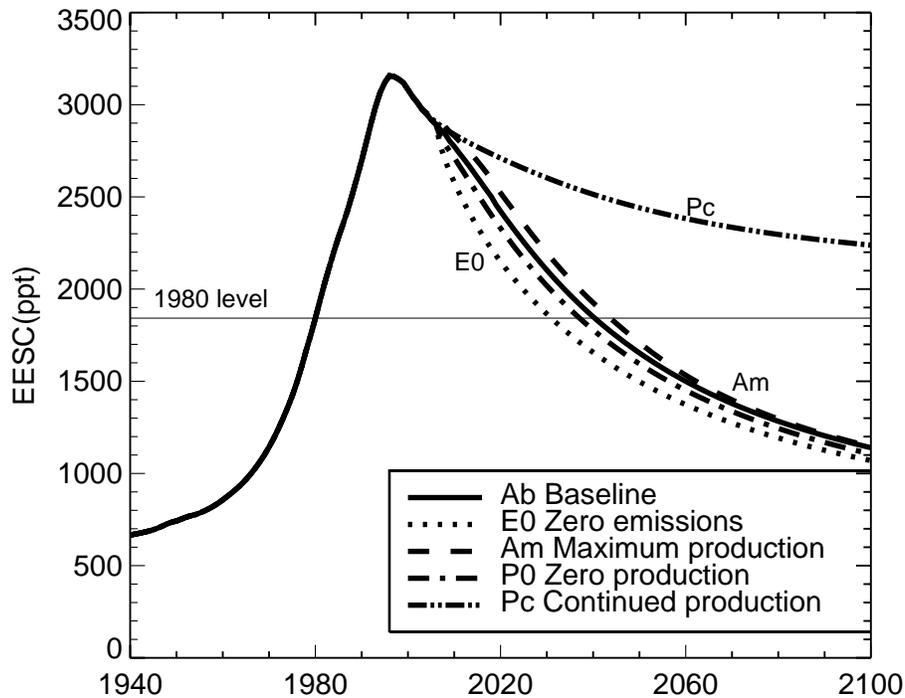


Figure 1-23. Estimates of future EESC based on the baseline scenario (Ab, solid line), the maximum scenario (Am, long-dashed line), and the hypothetical cases of zero emissions in 2003 and thereafter (E0) and zero production in 2003 and thereafter (P0) of all anthropogenic ODSs. Also shown are results from the scenario with continued ODS production in the future at 1999 rates (Pc), production that is substantially larger than allowed in the fully revised and amended Montreal Protocol. Additional description of these scenarios is found in Tables 1-13 and 1-14.

considered (Section 1.8.1), the EESC value in 1980 is calculated here to be 1.784 ppb, somewhat lower than in Madronich and Velders et al. (1999).

Future EESC and time-integrated EESC were calculated from halocarbon mixing ratios in selected scenarios (Table 1-17). For the baseline scenario (Ab), the calculated EESC reaches the 1980 level again in about 2044. This is a few years earlier than estimated in Madronich and Velders et al. (1999), 4 years longer than if production of all ODSs were to cease in 2003, and 10 years longer than if emission of all ODSs were negligible after 2003. In the maximum-emissions scenario (Am), EESC drops to the 1980 level in about 2048.

The cases provide a gauge of maximum potential reductions in EESC that would be achievable from further restrictions to future production or future production *and* emission of ODSs. Implementation of any new control measures, however, must include a consideration of costs and feasibility in addition to any atmospheric benefits, but those considerations are not discussed here. From the zero-production cases presented in Table 1-17, the influence of future ODS production allowances is apparent. Allowances for continued production of HCFCs, methyl bromide, and CFCs have the largest influence on integrated EESC in the future. The zero-emission cases quantify the contribution of future emissions plus future production to future EESC (relative to the Ab scenario) and suggest that ODS emissions from reserves of unemitted material will affect EESC as much as or more than the current future

ODS production allowances. The exception is methyl bromide, where reserves are presumed to be negligible; its influence on future EESC is primarily dependent upon the magnitude of future production.

To show the effect of noncompliance with the Montreal Protocol, the Pc scenario was constructed. This scenario demonstrates that with continued, constant production of ODSs, even at the reduced amounts reported for 1999, EESC remains well above the 1980 level through 2100 (Figure 1-23). In the Pc scenario, the integrated EESC through 2100 is about 3 times as high as in the baseline scenario (Table 1-17). The results from this scenario demonstrate clearly that atmospheric halogen will decline to pre-Antarctic-ozone-hole conditions only with adherence to future limits on production of ozone-depleting substances.

1.8.4 Uncertainty in the Baseline Scenario

The Ab scenario is constructed as a best guess for future ODSs emissions and mixing ratios. There are several sources of uncertainties in these quantities.

First, uncertainty in the Ab scenario arises because of our inability to predict future global HCFC production. Limits apply to production or consumption of HCFCs in countries operating under Article A5(1) of the Protocol only after 2016 based upon amounts produced or consumed in 2015.

Second, emissions of carbon tetrachloride not related to industrial CFC production are poorly character-

ized. Accordingly, it is difficult to know accurately how emissions not related to CFC production will change in the future.

Third, there are uncertainties in the release rates of ODSs to the atmosphere. In these scenarios, future annual emissions are calculated as a fraction of the unemitted reserves (or “bank”). This release fraction is based on an analysis of the quantities present in, and emitted from, the banks over the past decade (1990-1999). These release fractions are held constant from 2000 onward. Destruction of reserves or changes in the use patterns of ODSs would change the estimated release fraction and thereby the emissions and shape of the effective equivalent stratospheric chlorine (EESC) curve in the future, but less so for the integrated EESC values. For integrated EESC, when the emissions occur is less important; if the ODS reaches the stratosphere before the EESC value falls below the 1980 value (approximately 2040), it contributes to the integrated value.

Fourth, the size of reserves of produced but unemitted ODSs is uncertain. In creating scenario Ab, historical emissions were adjusted so that the calculated mixing ratios were consistent with measurements. These adjustments depend on the lifetimes and release rates to the atmosphere of ODSs, and they affect our estimates of present-day banks of unemitted ODSs. This is especially true for Halon-1211, considering the large uncertainty in reserves and in its global lifetime. To understand the influence these uncertainties have on the calculation of future EESC, selected sensitivity tests were performed and compared with the results of the Ab scenario. If the lifetime of Halon-1211 were 11 years, EESC would drop to the 1980 amount (integrated from 2002 onward) 2.0 years earlier, and the integrated EESC would be 7.9% smaller than compared with the Ab scenario in which a 16-yr lifetime for Halon-1211 is presumed. An additional future production for this halon totaling 22.9 Gg over the years 2000 to 2009 (from Fraser et al., 1999) and a 35-Gg larger bank in 2000 yields an increase in integrated EESC of 3.5% (integrated from 2002) and a delay in recovery of only 0.5 years. Smaller Halon-1211 reserves in 2000 of 65 Gg (Fraser et al., 1999; instead of 98 Gg in Ab) result in integrated EESC being -3.4% compared with the Ab scenario.

Fifth, a simple box model is used for the calculation of mixing ratios in scenarios, as has been done in past ozone Assessments. Advantages of the simple model are that it maintains consistency with past reports and is more easily interpreted than the 2-D and 3-D interactive models. Simple box models have many limitations that affect the accuracy of atmospheric mixing ratios calculated from emissions. For example, the exponential decay time constant of a trace gas in the absence of emissions is the same

as the trace gas lifetime in a one-box model. In the real atmosphere, however, this time constant can be different from the steady-state trace gas lifetime (Prather, 1996). Although such effects are thought to be small for long-lived ODSs, they are predicted to be substantial for some short-lived gases such as methyl bromide (Prather, 1997).

Sixth, accurate predictions of future halocarbon mixing ratios rely on an understanding of loss rates in the future (see Section 1.8.5). The composition of the atmosphere is changing, and this may alter the chemical or dynamical processes that regulate lifetimes of ODSs (Krol et al., 1998; Prinn et al., 2001; Butchart and Scaife, 2001).

1.8.5 Potential Influence of Future Climate Change on Halogenated Source Gases

About 80% of the equivalent chlorine in today’s atmosphere arises from direct anthropogenic release of ODSs. Climate change could influence future atmospheric amounts of these gases by affecting the rates at which these gases are removed from the atmosphere (Prinn et al., 2001; Butchart and Scaife, 2001). For CFCs, halons, and CCl₄, rates of atmospheric removal are governed by the flux of high-energy light in the stratosphere and the rate at which air is mixed through the stratosphere. If changes in climate were to affect rates of air transport through the stratosphere, trace gas lifetimes would be altered. The lack of predictive understanding of such changes does not allow a reliable estimate of whether lifetimes would become longer or shorter in the future in an atmosphere with elevated greenhouse gas abundances. For methyl chloroform, HCFCs, methyl halides, and other chemically reduced gases, climate change could influence loss rate through changes in mean global concentrations of the hydroxyl radical. This oxidant plays a key role in determining the lifetime of these important ozone-depleting substances. Amounts of this short-lived, but powerful atmospheric oxidant depend directly on humidity, sunlight, temperature, and the abundance of many different trace gases likely to be affected by climate change and human behavior in the future.

The remaining 20% of ODSs in today’s atmosphere arises from CH₃Cl, CH₃Br, and short-lived brominated gases (see Section 1.2.4 and Chapter 2). These gases are unique among ODSs because the predominant sources are believed to be nonindustrial, and climate change could affect the magnitude of sources for these gases. As a result there is less direct control over mixing ratios of these gases in the atmosphere. Our current understanding is limited for predicting even the net change in sources and sinks one might expect in the future for these methyl halides as

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a result of climate change or wide-scale land-use change. The influence of temperature on air-sea concentration differences have been identified recently (Groszko and Moore, 1998; King et al., 2000), but the relevance of this information to trace gas fluxes in and out of the future ocean has yet to be demonstrated.

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