

CHAPTER 2

Short-Lived Ozone-Related Compounds

Lead Authors:

M.J. Kurylo
J.M. Rodríguez

Coauthors:

M.O. Andreae
E.L. Atlas
D.R. Blake
J.H. Butler
S. Lal
D.J. Lary
P.M. Midgley
S.A. Montzka
P.C. Novelli
C.E. Reeves
P.G. Simmonds
L.P. Steele
W.T. Sturges
R.F. Weiss
Y. Yokouchi

Contributors:

D.M. Cunnold
E.J. Dlugokencky
J.W. Elkins
D.M. Etheridge
P.J. Fraser
D.E. Hartley
M.K.W. Ko
S. Madronich
E. Mahieu
W.A. Matthews
A. McCulloch
D.E. Oram
J.J. Orlando
S.A. Penkett
S.M. Schauffler
S.A. Yvon-Lewis

CHAPTER 2

SHORT-LIVED OZONE-RELATED COMPOUNDS

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SCIENTIFIC SUMMARY

Fluorinated and Chlorinated Compounds

- The Montreal Protocol and its Amendments have caused dramatic changes in industrial halocarbon emissions. For example, industrial sales of methyl chloroform (CH_3CCl_3) have dropped by more than a factor of 3 from 1990 to 1995, resulting in decreases in its tropospheric concentration over this same period, approaching 40%. This decline in tropospheric CH_3CCl_3 (about 40 to 42 parts per trillion (ppt) atomic chlorine (Cl) yr^{-1} in 1996) is one of the principal causes for the recent downturn in total tropospheric Cl.
- Rapid growth in the tropospheric concentrations of several hydrochlorofluorocarbons (HCFCs) has occurred throughout the 1990s as expected from continuation of previous uses and from use as replacements for chlorofluorocarbons (CFCs). As a result, tropospheric Cl from HCFC-22, -141b, and -142b was increasing in mid-1996 by about 11 ppt yr^{-1} and accounted for an equivalent of approximately 5% of the Cl present in long-lived tropospheric gases. This increasing contribution to tropospheric Cl offsets some of the 1996 decline in tropospheric Cl associated with the decreasing tropospheric burden of CH_3CCl_3 . This can be contrasted with the total tropospheric Cl growth rate throughout the 1980s, which exceeded 100 ppt yr^{-1} .
- Significant growth has also been recorded for some hydrofluorocarbons (HFCs). HFC-134a has increased throughout the 1990s from non-detectable levels to slightly greater than 3 ppt. HFC-23 (a byproduct of HCFC-22 production) has tracked the tropospheric concentration of HCFC-22 since 1980 and is growing at about 0.6 ppt yr^{-1} from a mid-1995 abundance of approximately 11 ppt.
- Based on the most recent analysis of the CH_3CCl_3 observational record (including a refinement in calibration), the atmospheric lifetimes (with respect to reactive removal by hydroxyl radicals (OH)) of CH_3CCl_3 , HCFCs, and HFCs, have been reduced by about 15% since the 1994 Assessment (WMO, 1995; see Table 2-1). The 1995 Intergovernmental Panel on Climate Change Assessment (IPCC, 1996) mostly reflected these revisions, with a slightly smaller correction factor of about 10%.
- Using the recommended lifetimes for HCFCs and HFCs, emissions calculated by industry from sales and use data are in accordance with the current global abundances of HCFC-22 and HFC-134a. For HCFC-141b and -142b, the industry data underestimate the current global abundances by factors of approximately 1.3 and 2, respectively.
- New measurements of, and improved calibrations for, methyl chloride (CH_3Cl), the largest natural source of atmospheric Cl, suggest that its global average mixing ratio is about 550 ppt, a slight revision of the 600 ppt given in the 1994 Assessment (WMO, 1995). Despite new information on CH_3Cl sources, their sum accounts for only 40 to 80% of the current atmospheric burden of CH_3Cl . New information on the marine production of CH_3Cl suggests a much lower oceanic source strength than previously assumed (constituting about 7 to 13% of the total source flux required to balance the removal of CH_3Cl by OH). These data imply that biomass burning now appears to be the largest known source of atmospheric CH_3Cl , approximately three times greater than the ocean source.
- The total Cl determined from the average tropical tropopause or lower stratospheric mixing ratios of the anthropogenic chlorocarbons methylene chloride (CH_2Cl_2), chloroform (CHCl_3), and tetrachloroethene (C_2Cl_4), and from phosgene (COCl_2 , a product of chlorocarbon breakdown in the atmosphere), indicates that these short-lived compounds contribute about 100 ± 20 ppt of Cl to the stratosphere, or about 3% of the total organic Cl.

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Methyl Bromide (CH₃Br)

- Recent measurements and intercomparison of calibration standards have confirmed that the average global mixing ratio of CH₃Br lies between 9 and 10 ppt, and that the interhemispheric ratio is 1.3 ± 0.1 (North/South), decreasing seasonally by as much as 0.2. Available data are not sufficient to determine the magnitude of CH₃Br trends since 1992.
- The amplitude of the seasonal behavior of CH₃Br shows wide geographical variability. The lack of an appreciable seasonal variation in the Southern Hemisphere (SH) suggests the existence of seasonality in other processes (sources or sinks) that offsets the signal for chemical removal by OH.
- Additional laboratory and shipboard measurements carried out since the 1994 Assessment (WMO, 1995) have changed our understanding of the ocean's role in the CH₃Br global budget. The ocean now appears to be a net sink, with an estimated net flux across the surface of about -21 Gg yr^{-1} , ranging from -3 to -32 Gg yr^{-1} . There is some evidence of seasonality in the saturation of CH₃Br at high latitudes, which suggests a close interplay between aquatic sources and sinks of CH₃Br and which further complicates narrowing the uncertainty in the global net flux across the ocean surface.
- New laboratory and field measurements and calculations utilizing global climatological data have increased the estimated total removal rates of CH₃Br. The magnitude of ocean uptake is -77 Gg yr^{-1} , with a range of -37 to -133 Gg yr^{-1} . Chemical removal in the ocean accounts for 70% of this estimate, with a newly identified biological ocean sink contributing the remaining 30%. Two different studies suggest a significant soil sink for CH₃Br. Although measured deposition velocities in similar soil types are consistent with each other, extrapolation to a global soil sink for CH₃Br yield estimates that differ widely due to utilization of different global soil type inventories. The best estimate for the soil sink for CH₃Br is -42 Gg yr^{-1} , with a range of -10 to -214 Gg yr^{-1} . Removal by atmospheric OH has been increased by 15% over the value in the 1994 Assessment (WMO, 1995) due to the impact of the recalibration of the CH₃CCl₃ data. The current estimate for OH removal is -86 Gg yr^{-1} , ranging from -65 to -107 Gg yr^{-1} . Thus the total removal rate of CH₃Br is -205 Gg yr^{-1} , with a range of -454 to -112 Gg yr^{-1} .
- No new important sources of CH₃Br have been identified. The total emission of CH₃Br from identified sources is 122 Gg yr^{-1} , with a range of 43 to 244 Gg yr^{-1} . The best-quantified source is fumigation, with a magnitude of 41 Gg yr^{-1} and a range of 28 to 64 Gg yr^{-1} . Other anthropogenic sources include biomass burning (20 Gg yr^{-1} , ranging from 10 to 40 Gg yr^{-1}) and leaded gasoline use (5 Gg yr^{-1} , ranging from 0 to 10 Gg yr^{-1}). Estimates of ocean emissions of order 60 Gg yr^{-1} can be directly deduced from the above estimates for ocean uptake and net ocean flux.
- The budget of atmospheric CH₃Br, calculated from our current understanding of sources and sinks, does not balance. Identified sinks (about 200 Gg yr^{-1}) outweigh identified sources (about 120 Gg yr^{-1}). The range in the imbalance is -315 to $+36 \text{ Gg yr}^{-1}$, obtained by combining estimated ranges for each of the sources and sinks. Because these ranges do not represent a statistical uncertainty, we cannot ascribe a probability to obtaining a balanced budget. Still, uncertainties in sources and sinks cannot easily explain the discrepancy.
- The current best estimate of the lifetime of atmospheric CH₃Br, calculated from losses within the atmosphere, to the ocean, and to soils, is 0.7 (0.4 to 0.9) years, contrasted with 1.3 (0.8 to 1.7) years given in the 1994 Assessment (WMO, 1995). The range is estimated by calculating the separate impacts of uncertainties in each of the sinks. The change from the 1994 Assessment is due primarily to both an increase in the ocean sink and the identification of a soil uptake, with a smaller contribution from the increase in the atmospheric removal rate. The Ozone Depletion Potential (ODP) for CH₃Br, calculated using the above lifetime and a bromine (Br)

efficiency factor of 58, is 0.4, with a range of 0.2 to 0.5. The ODP range is again calculated by considering the separate impacts of uncertainties in each of the parameters used for the ODP estimate. The bromine efficiency factor of 58 is greater than the value of 48 given in the 1994 Assessment due to improvements in our knowledge of stratospheric bromine chemistry.

Other Brominated Compounds

- Measurements of shorter-lived organic Br compounds (CH_2Br_2 , CHBr_3 , CH_2BrCl , CHBrCl_2 , CHBr_2Cl , and $\text{C}_2\text{H}_4\text{Br}_2$) indicate that these chemicals contribute 5 to 10 ppt Br to the tropospheric organic Br burden. However, such measurements have not been part of long-term monitoring programs and the data are sporadic in time and location, with a bias toward coastal and oceanic regions. Variable concentrations of these compounds (ranging from 1.0 to 1.7 ppt) have been reported at the tropical tropopause, but the paucity of data and the high variability make it difficult to quantify their contribution to reactive Br in the lower stratosphere.

Methane (CH_4) and Carbon Monoxide (CO)

- The current best estimate for the total atmospheric lifetime of CH_4 is 8.9 ± 0.6 years. The lifetime decrease since the 1994 Assessment (WMO, 1995) reflects the impact of the CH_3CCl_3 recalibration.
- The burden of atmospheric CH_4 continues to increase, but the rate of growth is declining. A growth rate of about 3 to 4 ppb yr^{-1} was reported for the 1996 to 1997 period, contrasting with an average increase rate of about 10 ppb yr^{-1} in the late 1980s. Apart from the anomalously low growth period after the 1991 eruption of Mt. Pinatubo, the above growth rate is the lowest since the mid-1940s. These lower growth rates are in contrast with the commonly used scenarios of future CH_4 emissions.
- Ground-based networks for carbon monoxide (CO) monitoring continue to expand, with many laboratories beginning new CO-monitoring programs. A recent intercomparison of measurements showed that large differences still exist between groups, which may be related to the calibration scales used in the analyses.
- The long-term increase in CO observed in the Northern Hemisphere (NH) until the mid- to late 1980s reversed at that time, with a steady average decrease of $2\% \text{ yr}^{-1}$ since 1990. This decrease continues today. No significant long-term trend in the SH has been deduced from measurements made over the past 20 years. However, periods of sharp decline in 1992 to 1993 and again in 1995 have yielded the lowest SH mixing ratios in the past two decades.

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

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

^a The numbers in parentheses represent lifetimes for removal by tropospheric OH scaled to the total atmospheric lifetime of CH₃CCl₃ (4.8 years) derived by Prinn *et al.* (1995), and adopting CH₃CCl₃ lifetimes for ocean removal of 85 years and stratospheric removal of 45 years (Kaye *et al.*, 1994). Adopting a shorter stratospheric removal time of 37 years (Prinn *et al.*, 1995; see also Volk *et al.*, 1997) yields a lifetime for CH₃CCl₃ removal by tropospheric OH of 5.9 years, which is within the uncertainty limits of the above (WMO, 1998) reference value.

^b Prinn *et al.*, 1995.

^c Miller *et al.*, 1998.

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

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

^f WMO (1998) CFC-11, H-1211, and CCl₄ lifetimes are lower than WMO (1995) values to take account of recent estimates based on stratospheric observations and models. Note that some calculations in later chapters of this 1998 Assessment were carried out before these WMO (1998) values were finalized and therefore used WMO (1995) values instead.

^g Butler *et al.*, 1998.

^h Not available or not applicable.

ⁱ Lifetime as calculated by Prinn *et al.* (1995). The adjustment time for CH₄ recovery would be somewhat longer due to CH₄ feedback on CO and OH (WMO, 1995).

2.1 INTRODUCTION

As indicated in past ozone assessments, knowledge of the distributions, trends, sources, and sinks of a wide range of atmospheric trace gases is required for understanding the present-day distribution of stratospheric ozone and to predict its future behavior in response to natural and anthropogenic forcings. These gases may also play a role in the forcing of climate change by altering the infrared radiative budget of the atmosphere. Such source gases are emitted as a result of naturally occurring processes or as a result of human activity and have lifetimes ranging from days to centuries. Chapter 1 of this Assessment focuses on “long-lived” source gases whose atmospheric photochemical destruction occurs predominantly (if not exclusively) in the stratosphere, and which thus tend to have lifetimes on the order of many years. The present chapter deals with the “short-lived” subset of ozone-related source gases that undergo significant chemical destruction in the troposphere, occurring primarily via reaction with tropospheric hydroxyl radicals (OH) or (as in the case of some iodine-containing compounds) via photolysis at wavelengths longer than 300 nanometers (nm). The lifetimes of these species tend to be shorter, ranging from days to several years. However, to keep the discussion together for all gases primarily destroyed through reaction with OH, the much longer-lived HFC-23 (CHF_3) also is included in this chapter. The present and future budgets of the source gases within this combined suite strongly influence the chemical composition of the Earth’s atmosphere and determine the atmospheric concentrations of free radicals, which define the magnitude of stratospheric ozone destruction. In particular, the combined data reviewed in Chapters 1 and 2 determine the loadings of stratospheric bromine (Br) and chlorine (Cl), which have played and continue to play a major role in the decreasing trends of stratospheric ozone.

In the following four sections of this chapter the measurements, distributions, sources, sinks, observed trends, and lifetimes of several subclasses of the short-lived source gases are reviewed. These subclasses include fluorinated and chlorinated compounds (the hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), other proposed chlorofluorocarbon (CFC) substitutes); methyl chloroform (CH_3CCl_3); brominated compounds (with a principal emphasis on methyl bromide (CH_3Br)); other halocarbons (such as the

chlorinated methanes and ethylenes as well as alkyl iodides); and other ozone-related compounds (methane (CH_4) and carbon monoxide (CO)). This information is used together with similar data for the long-lived source gases to determine the global halogen budgets that are given in Chapter 1. As in Chapter 1, we present model-calculated atmospheric lifetimes based on photochemical and kinetic data provided by laboratory studies. Whenever available, we also present lifetimes derived by inverse methods, in which atmospheric measurements are fit by model simulations that employ industrial emission estimates.

2.2 FLUORINATED AND CHLORINATED COMPOUNDS

2.2.1 Hydrochlorofluorocarbons (HCFCs) and Hydrofluorocarbons (HFCs)

2.2.1.1 SOURCES

Production of HCFCs and HFCs

Worldwide emissions of halocarbons have changed dramatically in recent years (Figure 2-1 and Figure 1-11 of Chapter 1) with the coming into force of the Montreal Protocol and its Amendments. The consumption (consumption = production + imports - exports) and most production of CFCs and CH_3CCl_3 were phased out in developed countries at the end of 1995. Exceptions include feedstock use and an allowance to supply the needs of developing countries whose own phase-out schedule begins with a freeze in 1999 and culminates in phase-out in 2010. This phase-out has stimulated a market for replacement products such as halocarbon alternatives and hydrocarbons, and alternative technologies such as aqueous cleaning systems. Conservation by means of improved design, recovery, and recycling has played a major role in reducing CFC emissions (UNEP, 1995). For certain applications, principally the servicing of existing refrigeration and air-conditioning equipment, the use of compounds with properties similar to those of the CFCs, such as HCFCs and HFCs, has been necessary in order to achieve the rapid phase-out of CFCs while permitting existing equipment to be operated for its useful economic life. However, because of their potential to deplete ozone, HCFCs are controlled under the Montreal Protocol as “transitional substances,” with a cap on consumption and

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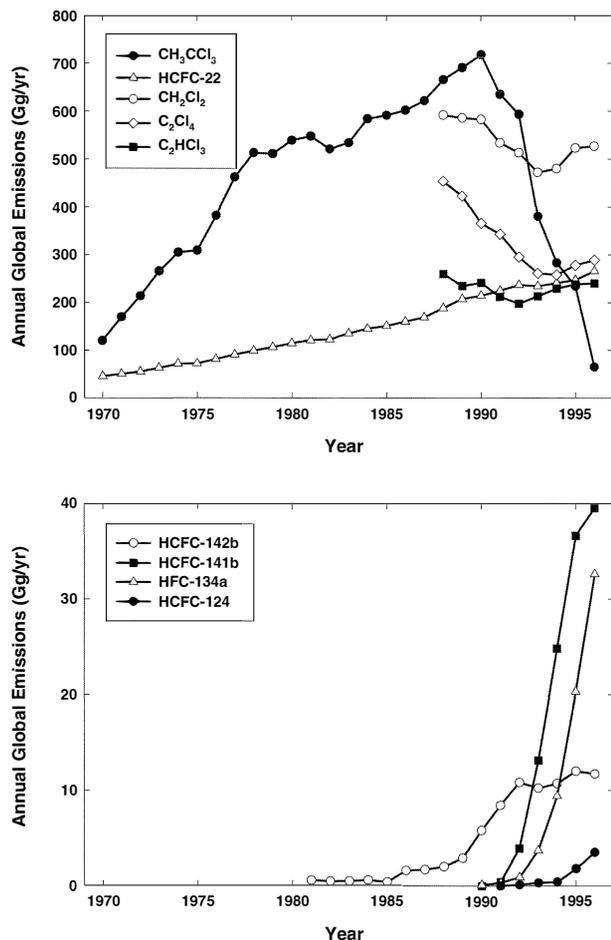


Figure 2-1. Annual global emissions of short-lived halocarbons (kt yr^{-1} , Gg yr^{-1}) estimated by industry from audited production, sales, and other data (AFEAS, 1998; Fisher *et al.*, 1994; Midgley and McCulloch, 1995; McCulloch and Midgley, 1996; and Midgley *et al.*, 1998). Note: There are no surveyed data for CH_2Cl_2 , C_2Cl_4 , and C_2HCl_3 prior to 1988.

a 2030 phase-out date in developed countries, and a cap on consumption and a 2040 phase-out date in developing countries.

HCFCs and HFCs are exclusively of industrial origin and their principal uses are in refrigeration and air conditioning (HCFC-22 (CHClF_2), HFC-134a (CH_2FCF_3)) and as foam-blowing agents (HCFC-142b (CH_3CClF_2), HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$)). The range of minor applications of HCFCs and HFCs includes propellants in medical and other aerosols, sterilants, and cleaning solvents. Certain HCFCs, notably HCFC-22

and HCFC-142b, are used as chemical feedstocks. That fraction of their production is captively converted and is not emitted to the atmosphere. HFC-23 is emitted into the atmosphere as a byproduct during the manufacture of HCFC-22.

The production and sales of HCFCs and HFCs for emissive uses are surveyed annually by the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS). AFEAS participants include all of the world's major producers, located in Europe, North America, and Japan, and their subsidiaries, giving virtually complete global coverage for HFCs and for most HCFCs (AFEAS, 1998). However, there is some evidence for additional HCFC-22 production, amounting to up to 10% of the total reported in the AFEAS survey (Midgley and Fisher, 1993; Fisher *et al.*, 1994; UNEP, 1997). The data presented in Figure 2-1 are annual global emission totals derived from industry reports and other data.

Production of HCFC-22 from companies reporting to AFEAS has increased steadily since the 1970s (AFEAS, 1998). The late 1980s were a period of faster growth in sales as HCFC-22 replaced CFCs in refrigeration. Approximately 95% of reported sales were made in the Northern Hemisphere (NH) through the period 1970 to date. Sales into dispersive uses in 1996 were 270 Gg, an almost fivefold increase since 1970 (AFEAS, 1998).

Industrial production of HCFC-141b and HCFC-142b increased markedly in the late 1980s and early 1990s as these HCFCs found use as replacements for CFCs and chlorinated solvents. Although production of HCFC-142b, initially mainly for feedstock use, began earlier than that of HCFC-141b, by 1996 the amount of HCFC-141b sold into dispersive uses was 3 times as much as HCFC-142b. Sales figures for that year were 121 Gg for HCFC-141b and 38 Gg for HCFC-142b, and indicate that more than 99% of sales of these compounds were in the NH (AFEAS, 1998). Sales of HCFC-142b in the last three years of reported data (1994 through 1996) have remained virtually constant.

Data have recently been reported on the production and sales of HCFC-124 (CF_3CHClF). Sales into dispersive uses in 1996 amounted to 4 Gg, again with over 99% in the NH (AFEAS, 1998).

The only HFC for which surveyed data has been reported by AFEAS is HFC-134a. Industrial sales of this "chlorine-free" refrigerant increased from zero in 1990 to 84 Gg in 1996 (AFEAS, 1998). The rapid growth in production and emission of HFC-134a and HCFC-

141b (and HCFC-124) is typical of newly introduced, industrial products and will gradually slow over a period of years to decades (McCulloch, 1994; Prather *et al.*, 1996).

Although demand for other HCFCs and HFCs such as HCFC-123 (CF₃CHCl₂), HFC-125 (CHF₂CF₃), HFC-143a (CH₃CF₃), and HFC-152a (CH₃CHF₂) have also increased lately as alternatives to CFCs in some applications, there are no production and sales data available at present.

Estimates of Emissions to the Atmosphere

The production and sales data reported by industry are used to generate annual emission estimates for each compound. This process, which has been extensively described (see, e.g., Midgley and Fisher, 1993; Fisher and Midgley, 1994; Midgley and McCulloch, 1995), involves the development of release algorithms based on the pattern of use and time scale of release from the various applications of each compound. This process is relatively straightforward for compounds with a single, well-defined use with immediate emissions, such as the solvent use of CH₃CCl₃, CH₂Cl₂, C₂Cl₄, and C₂HCl₃. It becomes less so for applications with longer and ill-defined delays between use of the compound and its

emission to the atmosphere. This is particularly critical for the release of blowing agents from closed cell foams, where a complex, multi-stage pattern of release takes place over decades. Thus emission estimates for compounds such as HCFC-142b and HCFC-141b have greater uncertainties principally because of difficulties in defining release from foams. Emissions of HCFCs, HFCs, and selected solvents estimated from global production data are given in Figure 2-1.

2.2.1.2 SINKS

Because they contain at least one carbon-hydrogen bond, HCFCs and HFCs react with OH. This oxidation occurs predominantly in the troposphere, where scavenging of water-soluble oxidation products prevents most of the reactive halogen carried by these trace gases from being transmitted to the stratosphere. Lifetimes with respect to oxidation by OH for most HCFCs are longer than several years (see Table 2-2), thereby permitting significant amounts of these compounds to reach the stratosphere (Lee *et al.*, 1995; Zander *et al.*, 1996). Once in the stratosphere, the propensity for a compound to degrade via photodissociation or chemical oxidation at stratospheric temperatures determines its contribution to the reactive halogen burden of the stratosphere.

Table 2-2. Calculated lifetimes.

	$\tau_{\text{OH}}^{\text{a}}$ (years)	$\tau_{\text{strat}}^{\text{a}}$ (years)	$\tau_{\text{atmos}}^{\text{b}}$ (years)
CH ₃ CCl ₃	5.7 ^c	45	4.8
HCFC-22	12.3	306	11.8
HFC-134a	14.1	377	13.6
HCFC-141b	10.4	81	9.2
HCFC-142b	19.5	372	18.5
HFC-23	255	5310	243

^a τ_{OH} and τ_{strat} are defined as the total atmospheric burden divided by the integrated loss due to reaction with OH in the troposphere and to reactive and photolytic losses in the stratosphere, respectively. Values of τ_{OH} were calculated using the scaling procedure suggested by Prather and Spivakovsky (1990) with the global OH concentration constrained by CH₃CCl₃ measurements. Values of τ_{strat} were calculated using the AER 2-D model.

^b
$$\frac{1}{\tau_{\text{atmos}}} = \frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{strat}}} + \frac{1}{\tau_{\text{ocean}}}$$
 where $\tau_{\text{ocean}} = 85$ yr for CH₃CCl₃. Table entries for other compounds assumed that there is no ocean uptake.

^c The 5.7-yr value of τ_{OH} for CH₃CCl₃ was derived using the 4.8-yr value of τ_{atmos} based on observations (Prinn *et al.*, 1995) together with a value of τ_{strat} of 45 yr and τ_{ocean} of 85 yr. Other values for τ_{OH} in this table are based on this 5.7-yr value. Prinn *et al.* (1995) used $\tau_{\text{strat}} = 37$ yr to calculate a slightly higher value of $\tau_{\text{OH}} = 5.9$ yr.

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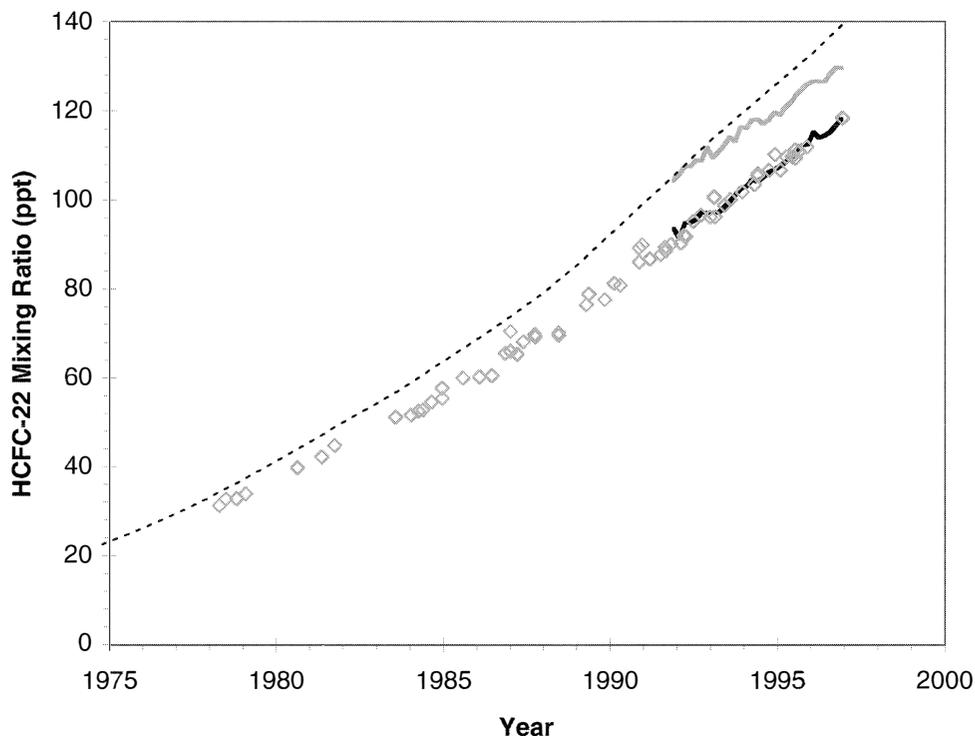


Figure 2-2. Ground-based measurements of HCFC-22 from the NH and SH. Bimonthly hemispheric means from flasks collected at four sites in the NH and three sites in the SH (solid lines, NH always greater than SH) (Montzka *et al.*, 1993; 1996a) are compared to data from analysis of the Cape Grim (Tasmania) Air Archive (CGAA; open diamonds) (Miller *et al.*, 1998). Also displayed are global mean surface mixing ratios calculated from estimates of global emission and a lifetime of 11.8 yr (dashed line). Emissions were estimated from countries reporting production (Midgley and Fisher, 1993; AFEAS, 1998) plus an additional 10% to account for production and emission elsewhere (Midgley and McCulloch, 1998).

Oxidation by OH in the troposphere is the predominant loss process for most HCFCs, and much less of the Cl they contain is released to the stratosphere as reactive halogen atoms when compared to similar emissions of the fully halogenated CFCs. At present, however, it is not possible to measure the mean global burden of OH to calculate explicitly loss rates owing to oxidation by OH. Instead, estimation techniques described in Section 2.2.3.2 allow us to deduce indirectly the OH burden within the troposphere. For short-lived compounds (lifetimes $\ll 1$ year), the spatial and temporal distribution of OH relative to the distribution of the compound itself will also play a role in the determination of global lifetime.

Another potential loss mechanism for these compounds is degradation in oceanic waters. Although small but significant amounts of CH_3CCl_3 undergo loss within the ocean (Butler *et al.*, 1991), this loss has been

estimated to be much less important for HCFC-22 ($\tau_{\text{ocean}} > 700$ yr) (Lobert *et al.*, 1995a).

Table 2-2 summarizes model-calculated lifetimes for several HCFCs, HFC-23, and HFC-134a. Lifetimes for removal by OH in the troposphere (τ_{OH}) are scaled (Prather and Spivakovsky, 1990) to the indicated lifetime for CH_3CCl_3 using laboratory-derived rate constants determined for the study compound and CH_3CCl_3 (DeMore *et al.*, 1997). This value of τ_{OH} for CH_3CCl_3 has been derived from a total atmospheric lifetime (τ_{atmos}) of 4.8 years (Prinn *et al.*, 1995), an oceanic removal lifetime (τ_{ocean}) of 85 years (Butler *et al.*, 1991), and a stratospheric removal lifetime of 45 years. Stratospheric lifetimes (τ_{strat}) have been calculated by the Atmospheric and Environmental Research, Inc. (AER) two-dimensional (2-D) model (see description in Prather and Remsberg, 1993).

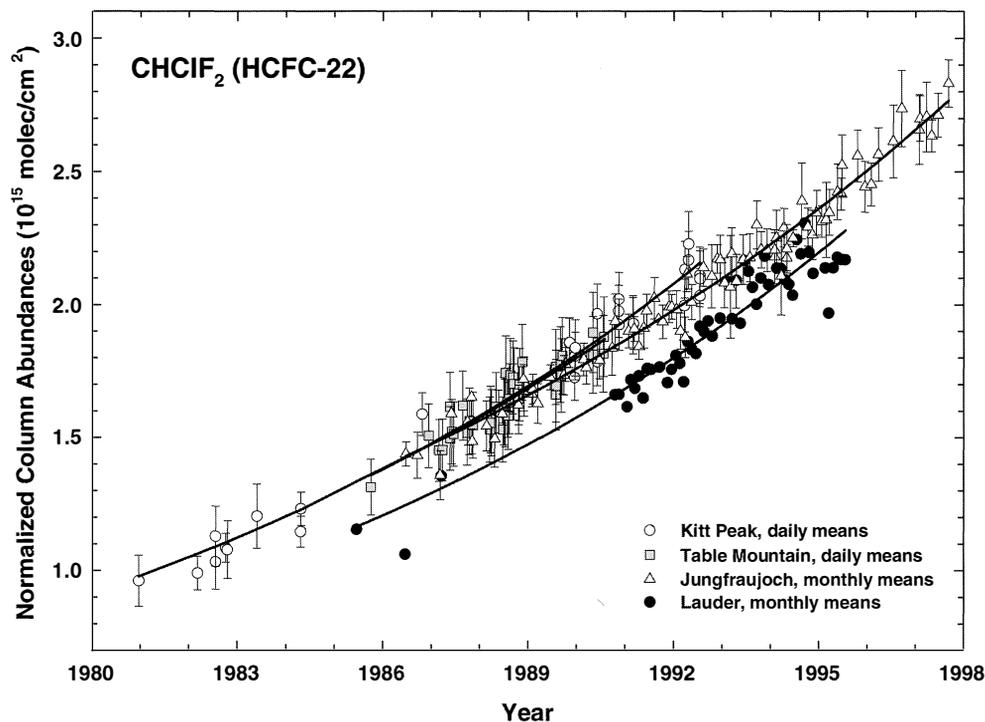


Figure 2-3. Trends (depicted by solid lines) in the normalized vertical column abundances of HCFC-22 monitored remotely at NH and SH sites, including Kitt Peak (31.9°N; open circles), Table Mountain (34.4°N; shaded squares), Jungfrauoch (46.5°N; open triangles), and Lauder (45.0°S; filled circles). The observed columns from the first three sites have been pressure-corrected (with respect to Lauder) to account for altitude differences among the various sites. Data include extensions of published work by Zander *et al.* (1994a), Irion *et al.* (1994), and Sherlock *et al.* (1997).

2.2.1.3 TROPOSPHERIC DISTRIBUTIONS AND TRENDS

HCFC-22 (CHClF₂)

Several new reports concerning long-term measurements of this compound, either from samples collected at ground-based stations or long-path absorption measurements, have appeared since the 1994 Assessment (WMO, 1995). These studies demonstrate that the abundance of HCFC-22 continues to increase throughout the global troposphere. Recent global HCFC-22 data (Montzka *et al.*, 1996a) indicate a global tropospheric mixing ratio in mid-1995 of 117 parts per trillion (ppt) and a global mean rate of increase between 1992 and 1996 of 5.0 ppt yr⁻¹ (Figure 2-2). The larger NH abundances (relative to Southern Hemisphere (SH) values) shown in Figures 2-2 and 2-3 for HCFC-22, and in subsequent figures for other compounds, reflect the

interhemispheric mixing time and the dominance of NH industrial sources for these chemicals.

Analyses of archived samples collected in Tasmania between 1978 and 1996 (Miller *et al.*, 1998) indicate a mixing ratio of 116.7 ppt in mid-1996, increasing at 6.0 ± 0.1 ppt yr⁻¹ (Figures 2-2 and 2-6). Results reported in this study also suggest that the abundance of HCFC-22 was approximately 35 ppt in 1978 at this site. These same authors report data from La Jolla, California, obtained from 1992 to 1997. The mid-1996 mean mixing ratio at this site was 132.4 ppt, increasing at a rate of 5.5 ppt yr⁻¹. The amounts of HCFC-22 observed in the modern atmosphere, and the steady increases observed at Tasmania since 1978, are reasonably well accounted for based upon industrial activity and a global lifetime for this compound of between 10 and 13 years.

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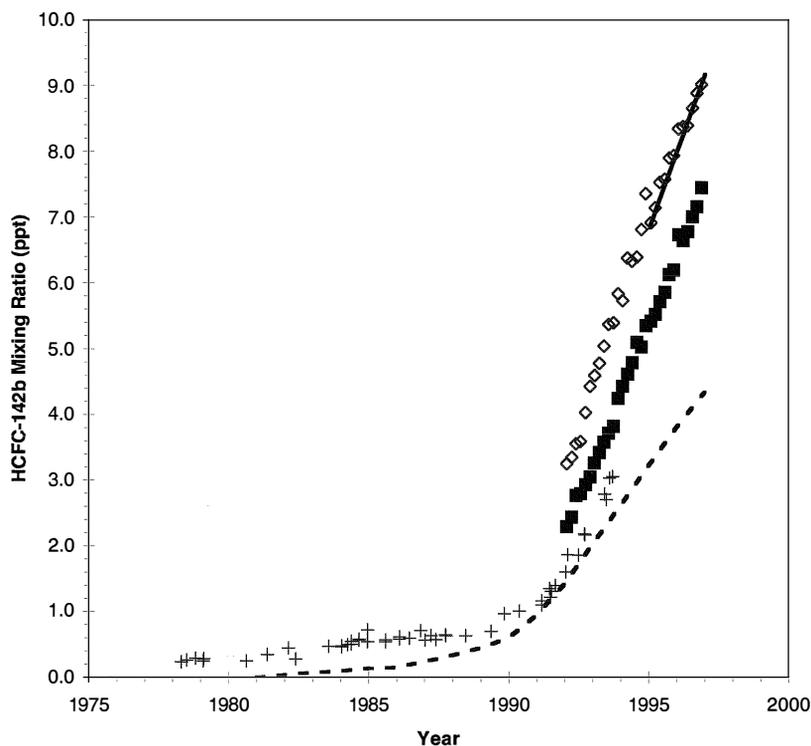


Figure 2-4. Ground-based measurements of HCFC-142b. NH means (flask sampling at four remote sites; open diamonds) and SH means (flask sampling at three remote sites, filled squares) (Montzka *et al.*, 1994, 1996a) are displayed along with results from the analysis of the Cape Grim (Tasmania) Air Archive (CGAA; plus symbols) (Oram *et al.*, 1995), and 6-hour measurements made at Mace Head, Ireland (smoothed to a solid line) (Simmonds *et al.*, 1998a). Also displayed are global-mean surface mixing ratios calculated from estimates of global emission (AFEAS, 1998) and a lifetime of 18.5 yr (dashed line) (Table 2-1).

Exchanges of real-air samples and standards between the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) and the Scripps Institution of Oceanography (SIO) reveal agreement to within 1% between these two laboratories for measurements of HCFC-22 (Miller *et al.*, 1998), suggesting improved calibration over earlier studies (Rasmussen *et al.*, 1980; Chen *et al.*, 1994) where significantly higher values were reported (see also Chapter 1 in Kaye *et al.*, 1994).

From a series of vertical column abundance measurements at the Lauder site (New Zealand; 45.0°S, 169.7°W, 370 m above sea level (asl)), Sherlock *et al.* (1997) derived an exponential rate of increase for HCFC-22 of $7.5 \pm 0.3\% \text{ yr}^{-1}$ over the period 1985 to 1994. This SH trend compares well with those reported for NH sites in the 1994 Assessment: $7.0\% \text{ yr}^{-1}$ at Kitt Peak, Arizona (31.9°N, 111.6°W, 2090 m asl) from 1980 to 1992 (Zander *et al.*, 1994a); $7.0\% \text{ yr}^{-1}$ at the Jungfrauoch,

Switzerland (46.5°N, 8.0° E, 3580 m asl) from 1986 to 1992 (Zander *et al.*, 1994a); and $6.7\% \text{ yr}^{-1}$ at Table Mountain, California (34.4°N, 117.7°W, 2258 m asl) from 1985 to 1990 (Irion *et al.*, 1994) (Figure 2-3). More recent measurements at the Jungfrauoch return an exponential rate of increase of $5.9 \pm 0.2\% \text{ yr}^{-1}$ for the entire period from 1986 to mid-1997. This rate is significantly lower than the $7.0 \pm 0.3\% \text{ yr}^{-1}$ trend derived over the shorter 1986 to 1992 time interval (Zander *et al.*, 1994a) and suggests that the growth rates derived from remote column measurements during the 1980s and early 1990s have not been sustained during recent years. This is also suggested by the 1992 to 1996 ground-based flask-sampling studies discussed earlier in this section.

Based upon the global OH burden estimated from the analysis of measurements of CH_3CCl_3 , Prinn *et al.* (1995) calculate a global atmospheric lifetime for HCFC-22 of $11.5 \pm 0.7 \text{ yr}$. The lifetime of 11.8 yr given in Table 2-2 (calculated using the scaling procedure

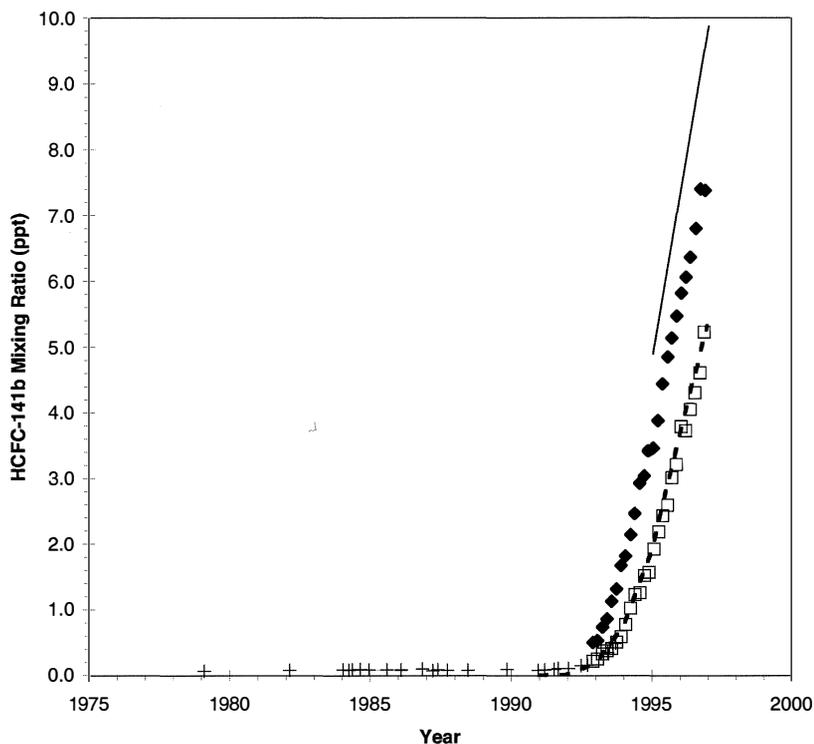


Figure 2-5. Ground-based measurements of HCFC-141b. NH means (flask sampling at four remote sites; filled diamonds) and SH means (flask sampling at three remote sites, open squares) (Montzka *et al.*, 1994, 1996a) are displayed along with results from the analysis of the Cape Grim (Tasmania) Air Archive (CGAA; plus symbols) (Oram *et al.*, 1995), and 6-hour measurements made at Mace Head, Ireland (smoothed to a solid line) (Simmonds *et al.*, 1998a). Also displayed are global-mean surface mixing ratios calculated from estimates of global emission (AFEAS, 1998) and a lifetime of 9.2 yr (dashed line) (Table 2-1).

described by Prather and Spivakovsky, 1990) is in good agreement with this value. Although lifetimes estimated from a budget analysis (comparison of measurements with emission estimates) do not differ significantly from 11.5 yr (Montzka *et al.*, 1993; Miller *et al.*, 1998), they have a larger uncertainty associated with them owing to the greater uncertainty in emissions estimated for HCFC-22 compared to CH_3CCl_3 (Midgley and Fisher, 1993).

HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$) and HCFC-142b (CH_3CCIF_2)

Observations of HCFC-141b and HCFC-142b reveal background tropospheric mixing ratios that are presently below 10 ppt but increasing rapidly on a relative basis since the early 1990s, and much higher amounts are observed in the NH when compared to the SH (Montzka *et al.*, 1994, 1996a; Oram *et al.*, 1995; Schauffler *et al.*, 1995; Simmonds *et al.*, 1998a; Shirai and Makide, 1998) (Figures 2-4, 2-5, and 2-6).

Data from a global ground-based flask sampling network indicate that the mean global tropospheric mixing ratio of HCFC-141b increased from 0.7 ppt in mid-1993 to 3.5 ppt in mid-1995; the rate of increase in mid-1995 was estimated at 1.9 ppt yr^{-1} (Montzka *et al.*, 1994, 1996a). From flask samples collected in the marine boundary layer of the eastern Pacific Ocean in April of 1993, mixing ratios for HCFC-141b of 0.83 ± 0.23 ppt in the NH and 0.28 ± 0.07 ppt in the SH were measured (Schauffler *et al.*, 1995). They also noted an increase in the midlatitude NH from 0.26 ppt in March 1992 to 1.41 ppt in September 1993. Similarly significant increases have been noted from in situ sampling and analysis of air at Mace Head, Ireland (Simmonds *et al.*, 1998a). In this study, a mean increase of 2.49 ppt yr^{-1} was noted for the period October 1994 through March 1997. The atmospheric mixing ratio reported at this site in January 1996 (the midpoint of the time series) was 7.38 ppt. A mean increase of $63 \pm 9\% \text{ yr}^{-1}$ for HCFC-141b was

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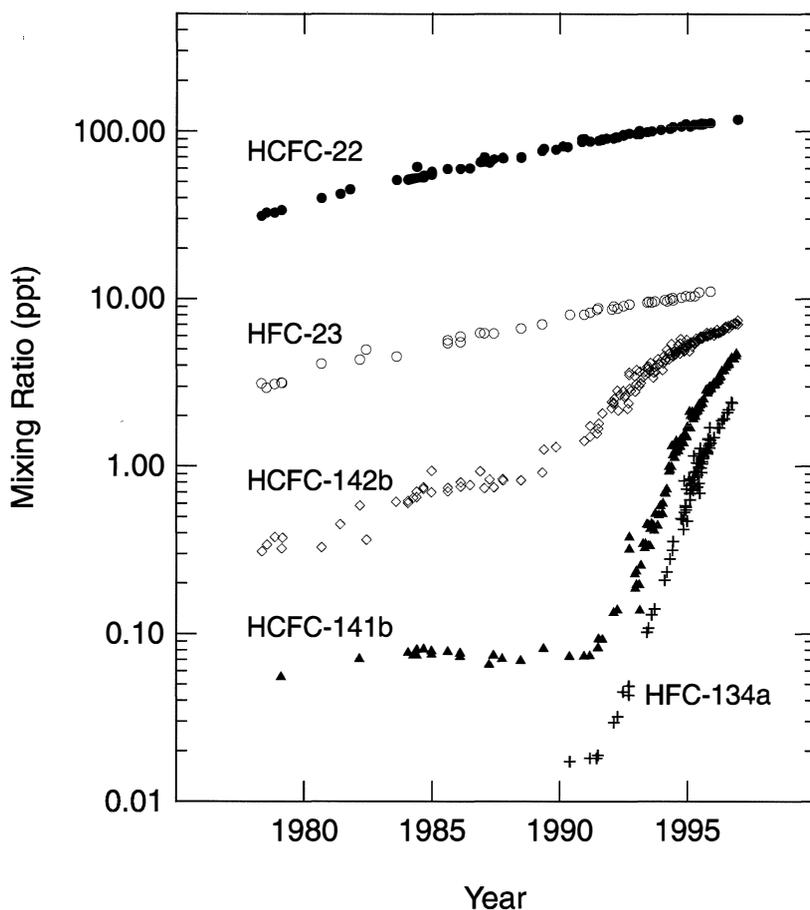


Figure 2-6. Ground-based measurements from Cape Grim, Tasmania, of HCFC-22 (filled circles) (Miller *et al.*, 1998), HFC-23 (open circles) (Oram *et al.*, 1998), HCFC-142b (open diamonds) (Montzka *et al.*, 1994, 1996a; Oram *et al.*, 1995), HCFC-141b (filled triangles) (Montzka *et al.*, 1994, 1996a; Oram *et al.*, 1995), and HFC-134a (plus symbols) (Montzka *et al.*, 1996a,b; Oram *et al.*, 1996) from the Cape Grim (Tasmania) Air Archive (CGAA) and ongoing sampling programs. For HCFCs -142b and -141b and HFC-134a, the data of Oram *et al.* (1995, 1996) have been scaled in this figure to the NOAA calibration scale.

calculated from measurements at Hokkaido, Japan, and Syowa Station, Antarctica, for the period from July 1995 to January 1997. The mean from these two stations was 5.7 ± 0.6 ppt in January 1997 (Shirai and Makide, 1998).

The mean global tropospheric mixing ratio of HCFC-142b increased from 4.3 ppt in mid-1993 to 6.6 ppt in mid-1995; the rate of increase has been fairly constant over the period 1992 to 1996 at 1.1 ppt yr^{-1} (Montzka *et al.*, 1994, 1996a; Elkins *et al.*, 1996). For the 30-month period preceding March 1997, Simmonds *et al.* (1998a) measured a mean increase of 1.16 ppt yr^{-1} at Mace Head, Ireland. They also report a January 1996 mixing ratio (the midpoint of the time series) of 8.0 ppt. Slightly larger increases of $1.6 \pm 0.1 \text{ ppt yr}^{-1}$ were determined from measurements made at Hokkaido, Japan, and Syowa Station, Antarctica (Shirai and Makide, 1998). The mean mixing ratio from these two sites was 10.4 ± 1.1 ppt in January 1997.

Data from archived air samples collected at Tasmania also reveal large increases for HCFC-141b and

HCFC-142b since 1978 (Oram *et al.*, 1995). For both HCFCs, small amounts (0.08 ppt for HCFC-141b in the 1980s, and 0.2 to 0.3 ppt for HCFC-142b in the early 1980s) were detected in the period before surveys report significant emissions from industrial production (AFEAS, 1998). Analysis of a smaller air archive dating back to 1987 from the NH (Elkins *et al.*, 1996) shows data supporting the observations of Oram *et al.* (1995) from Tasmania. More recently, large increases have been observed in the archive from Tasmania: in the period from 1992 to September 1993, mixing ratios of HCFC-141b increased from 0.08 ± 0.01 ppt to 0.46 ± 0.05 ppt. Similarly, between 1978 and 1993 the abundance of HCFC-142b increased from 0.20 ± 0.02 to 3.0 ± 0.3 ppt (Oram *et al.*, 1995).

The consistency observed by four independent laboratories reporting measurements for HCFC-141b is on the order of $\pm 5\%$ (Montzka *et al.*, 1994; Schauffler *et al.*, 1995; Oram *et al.*, 1995; Simmonds *et al.*, 1998a). For HCFC-142b, consistency within 5% is observed

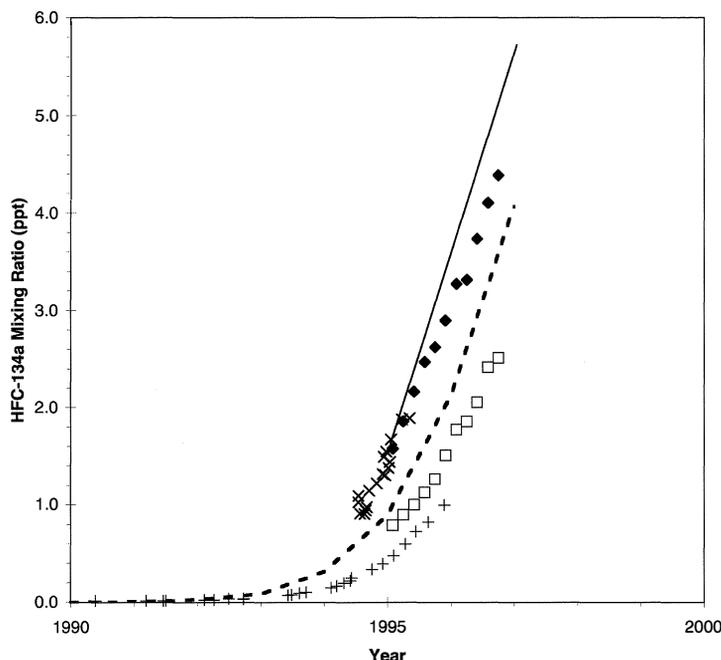


Figure 2-7. Ground-based measurements of HFC-134a. NH means (flask sampling at four remote sites; filled diamonds) and SH means (flask sampling at three remote sites, open squares) (Montzka *et al.*, 1994, 1996a) are displayed along with results from the analysis of the Cape Grim (Tasmania) Air Archive (CGAA; plus symbols) and Mace Head, Ireland (crosses) (Oram *et al.*, 1995), and 6-hour measurements made at Mace Head, Ireland (smoothed to the solid line) (Simmonds *et al.*, 1998a). Also displayed are global mean surface mixing ratios calculated from estimates of global emission (AFEAS, 1998) and a lifetime of 13.6 yr (dashed line) (Table 2-1).

between NOAA/CMDL and the University of Bristol (Simmonds *et al.*, 1998a); however, results reported by the University of East Anglia (UEA) (Oram *et al.*, 1995) are approximately 30% lower.

Despite these calibration uncertainties, preliminary estimates of emission (AFEAS, 1998) for both HCFC-141b and HCFC-142b lead to an underestimation of the amount observed in the atmosphere. Between 1990 and 1995, mixing ratios deduced from these emissions appear to underestimate the atmospheric burden of HCFC-142b by a consistent factor of between 1.6 and about 2 (Montzka *et al.*, 1994; Oram *et al.*, 1995; Simmonds *et al.*, 1998a; Shirai and Makide, 1998). For HCFC-141b, the discrepancy between observed mixing ratios and those calculated from emission estimates has decreased from a factor of about 2.0 in early 1993 to approximately 1.3 at the end of 1995 (Elkins *et al.*, 1996; Simmonds *et al.*, 1998a). For both compounds, these differences cannot be reconciled by simply adjusting estimates of global lifetime for these compounds. Depending on the

specific use of a chemical, the delay between production and release into the atmosphere can vary considerably. Hence the atmospheric abundances calculated from industrial emission estimates are highly sensitive to the use-model employed.

Measurements of these two HCFCs have also been made from samples collected in the stratosphere (Lee *et al.*, 1995). Observed relationships to nitrous oxide (N_2O) allowed for an estimate of the stratospheric chemical lifetime for HCFC-141b of 68 ± 11 years and a lower limit for HCFC-142b of 138 years (referenced to a chemical lifetime for N_2O of 110 years). These values are consistent with those estimated from models (Table 2-2).

HFC-134a (CH_2FCF_3)

Atmospheric measurements of HFC-134a indicate non-detectable levels before 1989-1990 in both hemispheres (<0.01 to 0.05 ppt) and large relative increases since that time (Figures 2-6 and 2-7) (Montzka

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et al., 1996b; Oram *et al.*, 1996). Analyses of samples in the Cape Grim (Tasmania) Air Archive (CGAA) revealed no detectable HFC-134a (<0.01 ppt) until May of 1990. Between 1992 and mid-1995, the concentration at Cape Grim increased exponentially at approximately 200% yr⁻¹ (i.e., by a factor of 3) (Oram *et al.*, 1996). Also noted in this study was an increase of 1.24 ± 0.11 ppt yr⁻¹ between July 1994 and May 1995 at Mace Head, Ireland. Slightly higher increases of 2.05 ppt yr⁻¹ were noted at Mace Head for a later period in a separate study (October 1994 to March 1997; Simmonds *et al.*, 1998a), consistent with accelerated emissions growth for this compound. These authors also report a mixing ratio at the midpoint of the time series (January 1996) of 3.67 ppt. Furthermore, mixing ratios calculated from industry emission estimates are in reasonable agreement with observed concentrations (Simmonds *et al.*, 1998a). A mean increase of 83 ± 6% yr⁻¹ for HFC-134a was calculated from measurements at Hokkaido, Japan, and Syowa Station, Antarctica, for the period from July 1994 to January 1997. The mean from these two stations was determined to be 5.9 ± 1.2 ppt in January 1997 (Shirai and Makide, 1998).

From samples collected at multiple sites in both hemispheres, a global tropospheric mean mixing ratio of 1.6 ppt was estimated for mid-1995, and mixing ratios in the NH were 2 times those observed in the SH (Montzka *et al.*, 1996a,b). Analyses of archived samples from the NH show increases above detection (0.05 ppt) in the period between 1989 and 1990. The rate of global increase was estimated for mid-1995 at 1.2 ppt yr⁻¹.

Mixing ratios reported by these three groups span a range of approximately 30%. However, results from a limited exchange of synthetic air samples, and from a comparison between ambient air measurements from Mace Head and Barrow, Alaska, suggest that the agreement between NOAA/CMDL and the University of Bristol is within 5% (Simmonds *et al.*, 1998a).

HFC-23 (CHF₃)

HFC-23 is produced primarily as a byproduct during the manufacture of HCFC-22 via the over-fluorination of chloroform (CHCl₃). Until recently, it was used as a starting material in the production of H-1301 (CBrF₃); however, such use has dropped to near zero in developed countries as a result of the phase-out of halon manufacture under the Montreal Protocol. Some

limited use continues in plasma etching processes, as a low-temperature refrigerant, and as a fire suppressant. Measurements made on the CGAA indicate that the HFC-23 mixing ratio has risen from approximately 2 ppt in 1978 to nearly 11 ppt by the end of 1995 (Oram *et al.*, 1998). As an expected result of its aforementioned source, HFC-23 exhibited long-term, near-linear growth through the 1980s and 1990s, similar to that of HCFC-22, with an abundance consistently about 10% of that of HCFC-22 (see Figure 2-6). This figure collectively shows data from the CGAA and ongoing sampling programs for HCFC-22, -141b, and -142b, and HFC-23 and -134a from Cape Grim, Tasmania.

2.2.1.4 TRIFLUOROACETIC ACID (TFA, CF₃C(O)OH)

Atmospheric breakdown of HFC-134a and certain other compounds containing a -CF₃ group, such as HCFC-123 and HCFC-124, will produce trifluoroacetyl halides (CF₃COCl or CF₃COF) that dissolve in water to give trifluoroacetic acid (TFA). Thus, TFA would then be present in rain or seawater. Reports suggest that growth is inhibited in certain plants following exposure to TFA at concentrations several thousands of times greater than expected in rain and snow from atmospheric oxidation of HCFCs and HFCs (Boutonnet *et al.*, 1998). TFA has already been detected at low levels in surface water, rain and tropospheric air samples (Frank *et al.*, 1996; Frank and Jordan, 1998; Zehavi and Seiber, 1996). The source of TFA in today's environment is uncertain but the breakdown of HCFCs and HFCs can only explain a tiny fraction of the observed levels because of the small quantities of these precursor compounds that have been produced and released to date (Kotamarthi *et al.*, 1998).

2.2.1.5 TOTAL Cl FROM HCFCs

A summary of our best estimates for concentrations and trends of HCFC/HFCs is given in Table 2-3. As can be seen for the most recent measurement period, tropospheric Cl in HCFCs was increasing by about 11 ppt yr⁻¹ and accounted for an equivalent of about 5% of the Cl present in long-lived anthropogenic trace gases in 1996. Of this 11-ppt yr⁻¹ increase, approximately 6 ppt yr⁻¹ is due to HCFC-22, associated primarily with a continuation of previous uses. The remainder is due to HCFC-141b and -142b, associated with their use as replacements for CFCs. This growth rate in tropospheric

Cl due to HCFCs can be contrasted to the current 40 to 42 ppt yr⁻¹ decline in tropospheric Cl associated with the decreasing atmospheric burden of CH₃CCl₃ (see Section 2.2.3.3). It also is considerably lower than the total tropospheric Cl growth rate throughout the 1980s, which exceeded 100 ppt yr⁻¹.

2.2.2 Other Proposed CFC Substitutes

As noted in Section 2.2.1.1, production and sales of other HCFCs and HFCs have increased lately.

Preliminary measurements now indicate very low levels of HCFC-123 and -124 and HFC-143a and -152a in the atmosphere. In addition to HCFCs and HFCs, perfluorocarbons and fluorinated ethers have been proposed as alternatives to CFCs, but they have not gone beyond the development stage to that of having significant emissions. Moreover, some have deliberately been chosen because they have such short atmospheric lifetimes that there is negligible flux of halogen to the stratosphere and their general environmental impact is reduced.

Table 2-3. Mixing ratios and trends for short-lived halocarbons at the Earth's surface. Mixing ratios are given as parts per trillion (ppt). Unless otherwise indicated, growth rates are estimated as the mean rate of change over the two years 1995 to 1996 and are in units of ppt yr⁻¹.

Compound	Mixing Ratio, Mid-1995 (ppt)	Mixing Ratio, Mid-1996 (ppt)	Growth (ppt yr ⁻¹)	Technique	Site	Reference
CH ₃ CCl ₃	110	97	-14	CMDL/in situ	Global	(a)
	102.5	88.7	-13.2	AGAGE/in situ	Global	(b)
CHClF ₂ (HCFC-22)	117	122	5.0	CMDL/flasks	Global	(a, c)
	110.8	116.7	6.0	AGAGE/flasks	40°S	(d)
	126.9	132.4	5.5	AGAGE/flasks	32°N	(d)
CH ₃ CCl ₂ F (HCFC-141b)	3.5	5.4	1.9	CMDL/flasks	Global	(a, e)
	————— 7.4 —————	—————	2.5	Univ. Bristol/in situ	53°N	(f)
CH ₃ CClF ₂ (HCFC-142b)	6.6	7.6	1.1	CMDL/flasks	Global	(a, e)
	————— 8.0 —————	—————	1.2	Univ. Bristol/in situ	53°N	(f)
CH ₂ FCF ₃ (HFC-134a)	1.6	3.0	1.4	CMDL/flasks	Global	(a, g)
	0.7	—————	0.64	UEA/flasks	40°S	(h)
	————— 3.7 —————	—————	2.1	Univ. Bristol/in situ	53°N	(f)
CHF ₃ (HFC-23)	10.7	—————	0.55	UEA/flasks	40°S	(i)

^a Montzka *et al.* (1996a), updated by Elkins *et al.* (1998); mean global estimate from measurements at five remote surface sites.

^b Prinn *et al.* (1995; 1998); mean global estimate from measurements at five remote surface sites.

^c Montzka *et al.* (1993), updated by Elkins *et al.* (1998); growth estimated as mean change over the period 1992 through 1996; mean global estimate from samples collected at seven remote surface sites.

^d Miller *et al.* (1998); growth estimated for mid-1996.

^e Montzka *et al.* (1994), updated by Elkins *et al.* (1998); mean global estimate from samples collected at seven remote surface sites.

^f Simmonds *et al.* (1998a); mean growth rate reported over the period between October 1994 and March 1997; mixing ratio reported was estimated for January 1996.

^g Montzka *et al.* (1996b), updated by Elkins *et al.* (1998); mean global estimate from samples collected at seven remote surface sites.

^h Oram *et al.* (1996); growth rate estimated from data through 1995 only.

ⁱ Oram *et al.* (1998).

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2.2.3 Methyl Chloroform (CH₃CCl₃)

2.2.3.1 SOURCES

CH₃CCl₃ is used primarily as a cleaning solvent. It is also used as a chemical feedstock, but that fraction of its production is not emitted into the atmosphere. Industrial sales of CH₃CCl₃ have declined rapidly in recent years; surveys of the world's major producers show that sales were 220 Gg in 1995, less than one-third of the amount reported for 1990, the year of peak production (Midgley and McCulloch, 1995; Midgley *et al.*, 1998). In 1996 there was no new production for sales into emissive uses in the developed world. Total consumption of CH₃CCl₃ in developing countries operating under Article 5 of the Montreal Protocol was approximately 30 Gg in 1994 (UNEP, 1997). It has been estimated that these requirements were mostly met by material exported from developed countries and that production capacity in developing countries lies well below this figure (Midgley and McCulloch, 1995). Consumption in developing countries is frozen in 2003 and phased out in 2005.

Emission estimates are most accurate for solvents such as CH₃CCl₃, because release from solvent uses is immediate. Estimated global emissions of CH₃CCl₃ are shown in Figure 2-1.

2.2.3.2 SINKS

CH₃CCl₃ is destroyed primarily through its reaction with OH in the troposphere. Measurements of the atmospheric burden and distribution of CH₃CCl₃ have been used to indirectly determine global average OH concentrations by different estimation techniques. These estimation techniques incorporate model calculations and inverse methods. In the hypothetical situation in which emission and loss rates for a compound are known, it is straightforward to calculate the concentration of that gas over time with an atmospheric model (e.g., Hartley *et al.*, 1994). However, for gases oxidized primarily by OH, the results of such calculations are affected by uncertainties in modeling the global OH burden. For these gases, loss rates are determined by inverting the calculation: estimates of emission and atmospheric observations are reconciled with an appropriate loss rate. These inverse methods are used to find an OH field that optimally "fits" the known emissions and the observations of the gas. This has been the focus of recent

studies using inverse methods with CH₃CCl₃ observations and emissions (Prinn *et al.*, 1995).

Three different inverse methods are common in atmospheric modeling. The "trend" method generates an optimal fit of OH based upon estimated emissions and the observed trend of the gas. This method is insensitive to the absolute accuracy of the measurement calibration. The other common techniques are sensitive to the calibration accuracy. They include finding an OH field that optimally fits atmospheric observations given estimates of emission (the content method), and finding an OH field that optimally fits the measured concentrations at different latitudes relative to the global average (the gradient method). Thus, using all three methods gives a measure of consistency. The latest estimates of OH are consistent in all three methods (Prinn *et al.*, 1995), yielding a tropospheric-average OH concentration of $(9.7 \pm 0.6) \times 10^5 \text{ cm}^{-3}$. When combined with the smaller stratospheric and oceanic sinks, these estimates correspond to a total atmospheric lifetime of 4.8 ± 0.3 years for CH₃CCl₃.

Emission estimates and measurements of HCFCs and HFCs also can allow for independent estimates of OH (e.g., Miller *et al.*, 1998). The ability of this approach to constrain estimates for the global OH burden will likely vary depending upon the accuracy and precision of emission estimates and measurements, and the lifetime of the gas relative to its period of use.

2.2.3.3 RECENT TRENDS

Data for CH₃CCl₃ from two ground-based global sampling networks have been updated since the 1994 Assessment (WMO, 1995) (Prinn *et al.*, 1995, 1998; Montzka *et al.*, 1996a; Elkins *et al.*, 1998). In both studies, significant declines in the global tropospheric abundance of CH₃CCl₃ were noted (Figure 2-8, Table 2-3). Whereas the mixing ratio of this gas increased before 1991, it decreased after 1991 and the rate of decline was between 13 and 14 ppt yr⁻¹ by mid-1996. Similar declines have been noted at Mace Head, Ireland (Simmonds *et al.*, 1996), and at a less remote site in the eastern United States (Hurst *et al.*, 1997). For example, mixing ratios at Mace Head have declined from a peak maximum of 153 ppt in 1990 to 93 ppt in 1996, or less than observed when measurements were first made in 1978 (Derwent *et al.*, 1998). Hurst *et al.* (1998) observed a 72% decrease in the atmospheric variability of CH₃CCl₃ during 1995 through 1997 at a tall (610-m) transmission

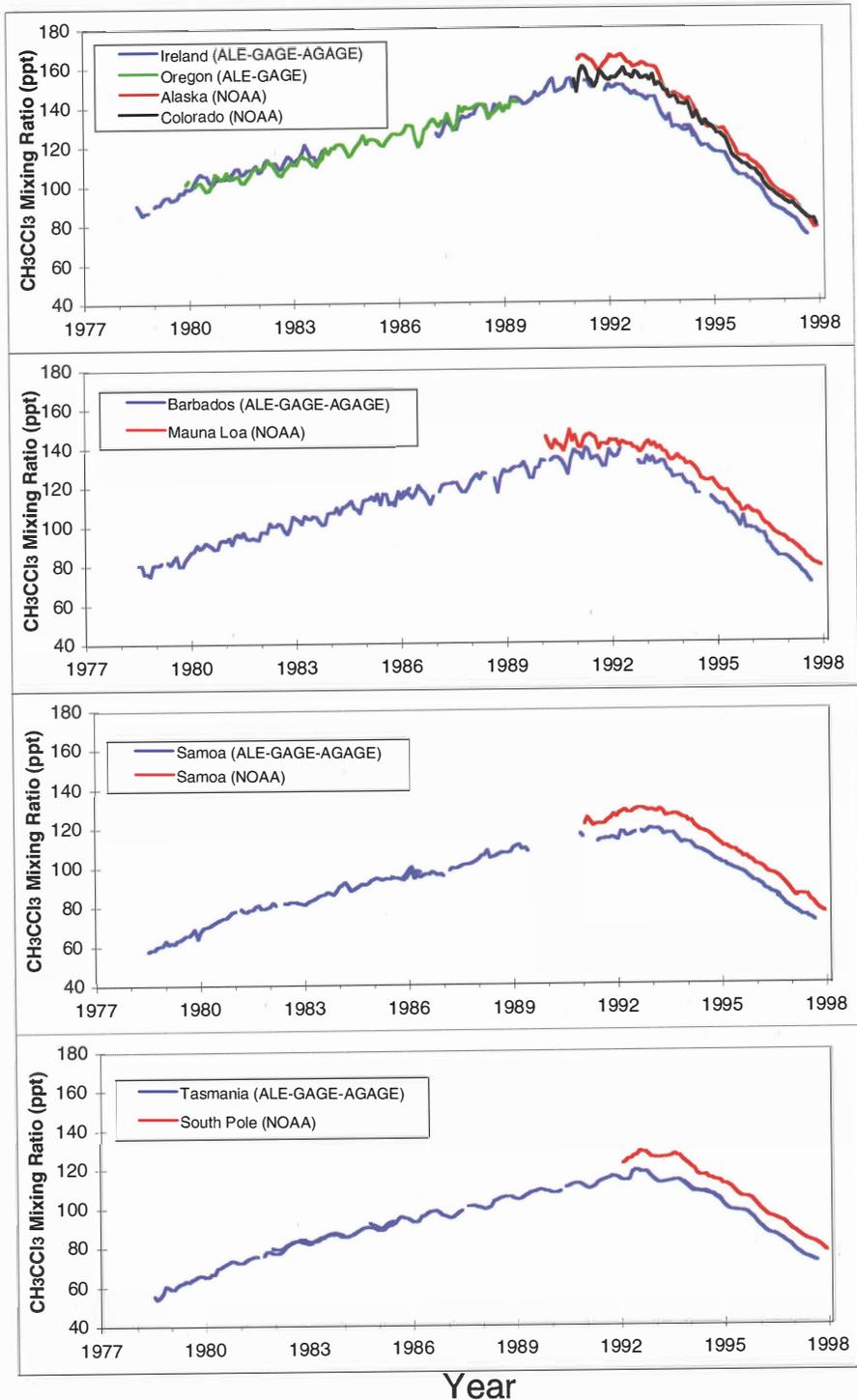


Figure 2-8. Monthly mean CH_3CCl_3 mixing ratios from the NOAA/CMDL (Montzka *et al.*, 1996a; Elkins *et al.*, 1998) and ALE/GAGE/AGAGE (Prinn *et al.*, 1995, 1998) global sampling networks. The Advanced Global Atmospheric Gas Experiment (AGAGE) is the successor to GAGE, which in turn was successor to the Atmospheric Lifetime Experiment (ALE).

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tower in eastern North Carolina, U.S. (35°21'N, 77°23'W, 505 m), which they attribute to reductions in emissions.

The decline in mixing ratio for this gas and the changes observed in its global tropospheric distribution are consistent with reduced NH emissions (Midgley and McCulloch, 1995; Bakwin *et al.*, 1997) and a global lifetime of 4.8 ± 0.3 years (Prinn *et al.*, 1995). This lifetime estimate is lower than in previous assessments owing to new gas calibration procedures incorporated by the Advanced Global Atmospheric Gas Experiment (AGAGE) program (Prinn *et al.*, 1995). With this improvement, good consistency is now observed between estimates of lifetime based on techniques that are calibration-dependent and those that are calibration-independent. This was not true for earlier, longer estimates of CH_3CCl_3 lifetime (Bloomfield *et al.*, 1994). Despite these revisions, measurements of CH_3CCl_3 from two independent global sampling networks (AGAGE and NOAA/CMDL) still disagree by about 10%; estimates of the global burden at the Earth's surface in mid-1996 from these networks range from 89 ppt (Prinn *et al.*, 1995, 1998) to 97 ppt (Montzka *et al.*, 1996a; Elkins *et al.*, 1998) (Table 2-3).

Volk *et al.* (1997) estimate a stratospheric lifetime (i.e., total burdened stratospheric loss) for CH_3CCl_3 at 34 ± 7 years based on a CFC-11 lifetime of 45 years and measured mixing ratios above the tropopause. Model calculations suggest a stratospheric lifetime for CH_3CCl_3 of 45 years (Table 2-2) (Kaye *et al.*, 1994). Such differences reflect the sensitivity of the stratospheric lifetime calculated for compounds removed by OH to the altitude at which the tropopause is placed.

2.2.4 Methyl Chloride (CH_3Cl)

The most abundant halocarbon in the atmosphere is CH_3Cl . Numerous results of ambient samples collected during various measurement campaigns have been published during the past 20 years and range in mole fraction from 300 to 1100 ppt. In previous assessments the average global mixing ratio was reported as approximately 600 ppt. Recent results from shipboard and airborne programs suggest a north/south gradient (Koppmann *et al.*, 1993; Moore *et al.*, 1996b), seasonality, and tropospheric vertical structure (Blake *et al.*, 1997). Use of these and other archived data gives a global average CH_3Cl mixing ratio of 550 ± 30 ppt. In contrast Khalil (1998) and Khalil and Rasmussen (1998a) report

consistently higher values (global average of 597 ppt). This suggests that there may exist unresolved calibration issues. Khalil and Rasmussen (1998a) also show evidence for a slight decrease (by about 4%) in global CH_3Cl levels between 1981 and 1997 at the Cape Meares, Oregon, site. No other studies have indicated temporal changes, and future determination of possible trends will need to address the aforementioned calibration issues.

The main known sources of CH_3Cl are from biomass burning (Crutzen *et al.*, 1979), emission from ocean surface waters (Singh *et al.*, 1983), and wood-rotting fungi (Watling and Harper, 1998). A considerable amount of new information is available with respect to the marine production of CH_3Cl , suggesting a much lower source strength than had been previously assumed (Moore *et al.*, 1996b). Extrapolation from measurements in the northwest Atlantic and Pacific Oceans suggests emission of CH_3Cl at lower latitudes from warmer waters (0.4 to 0.6 Tg yr^{-1}), but uptake at higher latitudes by colder waters (0.1 to 0.3 Tg yr^{-1}), yielding a global net oceanic source strength of 0.2 to 0.4 Tg yr^{-1} . Based on these estimates, the net oceanic emission would only account for some 7 to 13% of the sources needed to balance the calculated sink (discussed below as being about 3 Tg yr^{-1}).

Rudolph *et al.* (1995) estimated that biomass burning emissions may represent up to half of the CH_3Cl emissions, whereas Graedel and Keene (1995) have suggested that natural sources dominate over biomass burning and anthropogenic emissions. The most recent estimates of CH_3Cl emissions from biomass burning are approximately $1.0 \pm 0.3 \text{ Tg yr}^{-1}$ (Andreae *et al.*, 1996; N.J. Blake *et al.*, 1996), with substantial uncertainties still persisting due to the lack of data from tropical forest fires. Wood-rotting fungi appear to be a potentially significant global source of CH_3Cl . Watling and Harper (1998) estimate a global emission of 0.16 Tg yr^{-1} from fungal species of the *Hymenochaetaeaceae*. They suggest that actual emissions could be as much as an order of magnitude greater if fungal uptake of chloride from soil and leaf litter also occurs. Production from non-Hymenochaetaeaceous fungi has yet to be studied in detail. Given the recent downward revision of the marine source and the small size of the industrial emissions (0.2 to 0.4 Tg yr^{-1}), primarily from waste incineration (Graedel and Keene, 1995), biomass burning may be the single largest source of atmospheric CH_3Cl , followed by ocean emissions and fungal production.

Table 2-4. Lifetimes for miscellaneous halocarbons^a.

Compound	Lifetime	Major Removal Process
CH ₃ Cl	1.3 years	OH reaction
CH ₂ Cl ₂	5 to 6 months ^b	OH reaction
CHCl ₃	~6 months	OH reaction
C ₂ HCl ₃	~1 week	OH reaction
C ₂ Cl ₄	3 to 4 months	OH reaction
COCl ₂	70 days ^c	Wet Deposition
CH ₃ I	4 days at surface 1.5 days at 10 km ^c	Photolysis
C ₂ H ₃ I	Similar to CH ₃ I ^c	Photolysis
CH ₂ ClI	~100 minutes ^c	Photolysis
CH ₂ I ₂	2.5 minutes ^c	Photolysis
CH ₃ CHICH ₃	~16 hours ^c	Photolysis
CH ₃ CH ₂ CH ₂ I	~1 day ^c	Photolysis
CF ₃ I	1 day ^d	Photolysis

^a Unless otherwise stated, lifetimes are calculated from the reaction rates with OH (De More *et al.*, 1997), assuming an OH concentration of $9.7 \times 10^5 \text{ cm}^{-3}$ (Prinn *et al.*, 1995), using an average temperature of 277 K (Prather and Spivakovsky, 1990).

^b Kindler *et al.*, 1995.

^c Roehl *et al.*, 1997.

^d Rattigan *et al.*, 1997.

The main removal process for CH₃Cl is reaction with OH. Based on an average OH concentration of $9.7 \times 10^5 \text{ cm}^{-3}$ (Prinn *et al.*, 1995), CH₃Cl has an atmospheric lifetime of approximately 1.3 years (see Table 2-4). This estimate does not include other unquantified potential losses, such as attack by Cl atoms, as hypothesized by Keene *et al.* (1996), or uptake by soils as observed by Khalil (1998). Transport to the stratosphere accounts for approximately 1% of CH₃Cl removal (Graedel and Crutzen, 1993). Given an average global mixing ratio of 550 ppt, a global burden of 4.3 Tg is calculated which, in conjunction with the estimated lifetime, implies a global turnover rate of about 3 Tg yr⁻¹.

It should be noted that the sum of quantified sources given above (biomass burning, marine emissions, fungal production, and industrial emissions) is only 1.2 to 2.5 Tg yr⁻¹, well short of the rate at which CH₃Cl is oxidized by OH. This inconsistency between the sources and sinks of CH₃Cl is very similar to the budget imbalance noted for CH₃Br in Section 2.3.1.5. It is

possible that terrestrial emissions are important. Higher concentrations have indeed been observed over land (Khalil and Rasmussen, 1998a). The possibility of in situ production, such as the oxidation of dimethyl sulfide by Cl atoms (Langer *et al.*, 1996), has also been suggested.

2.2.5 Methylene Chloride (CH₂Cl₂)

CH₂Cl₂ is present in the atmosphere due to a variety of applications in industrial and consumer products ranging from food processing to paint stripping. McCulloch and Midgley (1996; updated by P.M. Midgley, M & D Consulting, Germany, private communication, 1998) estimate global emissions from audited sales data at 592 Gg and 527 Gg for 1988 and 1996, respectively (Figure 2-1), with over 90% of sales in the NH. The 1995 NH usage was 486 Gg, whereas usage in the SH was 37 Gg. NH and SH values of 40 to 50 ppt and 15 to 20 ppt, respectively, were obtained during a northern and southern Atlantic cruise and a northern and southern Pacific cruise (Koppmann *et al.*, 1993; Atlas *et al.*, 1993). Elkins *et al.* (1996) observed similar results from several NH and SH ground-based sites. The main removal process for CH₂Cl₂ is by reaction with OH. Assuming an average global OH concentration of $9.7 \times 10^5 \text{ cm}^{-3}$ yields an atmospheric lifetime of 5 to 6 months for CH₂Cl₂. Elkins *et al.* (1996) report seasonal variations in both hemispheres (six months out of phase), with maximum NH concentrations during winter. Graedel and Keene (1995) estimate that about 2% of CH₂Cl₂ emissions reach the stratosphere. Measurements of CH₂Cl₂ near the tropical tropopause in 1992 averaged 14.9 ± 1.1 ppt (Schauffler *et al.*, 1993). No long-term measurement data have been reported for CH₂Cl₂ but, with fairly flat sales figures since 1991, no temporal trend is expected.

2.2.6 Chloroform (CHCl₃)

CHCl₃ emissions arise from a variety of anthropogenic activities including coal combustion, waste incineration, and industrial processes. Emissions may occur during the deliberate production and use of the material or when it is present as a significant byproduct of an industrial process such as from paper-making or waste-water treatment. There are no audited production data for CHCl₃ because of multiple sources, some of which are hard to quantify. According to a recent detailed

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study (Aucott *et al.*, 1998) industrial emissions are much lower than previously thought (Khalil and Rasmussen, 1983), totaling about 60 Gg yr⁻¹, of which pulp and paper manufacture contributed about 30 Gg yr⁻¹, and wastewater treatment about 20 Gg yr⁻¹. It also has been suggested that termites could be a significant source of CHCl₃, 3 to 30 Gg yr⁻¹ (Khalil *et al.*, 1990). Frank and Frank (1990) and Hoekstra and De Leer (1993) have demonstrated production of CHCl₃ from soils, and Hoekstra *et al.* (1998) have shown production by fungi. An ocean source of around 0.36 Gg yr⁻¹ was estimated by Khalil and Rasmussen (1983), but this number has not been updated recently. No significant CHCl₃ emissions were observed during NASA's 1992 Transport and Atmospheric Chemistry near the Equator-Atlantic (TRACE-A) biomass burning study conducted in Africa and South America (N.J. Blake *et al.*, 1996).

A seasonal cycle in phase with CH₂Cl₂, tetrachloroethene (C₂Cl₄), and CH₃Cl is reported for CHCl₃ using three years of remote-site flask data (Elkins *et al.*, 1996). Elkins *et al.* (1996) reported a NH concentration range of 10 to 15 ppt whereas the SH was 5 to 7 pptv. Similar results were obtained on a cruise in the tropical Pacific (Atlas *et al.*, 1993). Khalil and Rasmussen (1998b) report NH concentrations of about 12 to 38 ppt at coastal sites, and 10 to 15 ppt in the SH, again suggesting calibration differences between groups. Concentrations at remote inland sites were higher again, up to 50 ppt. The NH scatter is significantly greater for CHCl₃ than for the other gases mentioned, supporting the suggestion that CHCl₃ has multiple uncoupled sources. Khalil and Rasmussen (1998b) found no significant long-term trend over 9 years at six different sites, although there were substantial year-to-year variations. Kindler *et al.* (1995) estimate that about 2% of CHCl₃ emissions are destroyed in the stratosphere. Measurements of CHCl₃ near the tropical tropopause in 1992 averaged 3.1 ± 0.7 ppt (Schauffler *et al.*, 1993).

The main removal process is reaction with OH. Assuming an average OH concentration of 9.7 × 10⁵ cm⁻³ yields an atmospheric lifetime for CHCl₃ of approximately 6 months (Table 2-4). If we exclude the ocean source and use the recent estimates of anthropogenic (i.e., industrial) emissions, the source total is inconsistent (i.e., too small) with a lifetime for CHCl₃ slightly longer than that for CH₂Cl₂ and atmospheric concentrations approximately one-third those of CH₂Cl₂. Inclusion of a large estimate for either the ocean or soil source (Khalil and Rasmussen, 1983) shifts this source/

burden inconsistency in the direction of too high a total source strength. More accurate quantification of these sources is clearly required.

2.2.7 Trichloroethene (C₂HCl₃)

The major source of C₂HCl₃ is from industrial usage as a degreasing agent. McCulloch and Midgley (1996; updated by P.M. Midgley, M & D Consulting, Germany, private communication, 1998) report global emissions estimated from audited sales for 1988 and 1996 of 260 Gg and 240 Gg (Figure 2-1). All but about 2% of the sales are in the NH. The main removal process is with OH. Assuming an average OH concentration of 9.7 × 10⁵ cm⁻³, the atmospheric lifetime for C₂HCl₃ is about 1 week (Table 2-4). From weekly samples collected at Alert, Canada, between early 1992 and mid-1994, Yokouchi *et al.* (1996) report winter/summer NH concentration ratios of approximately 60, with winter peak concentrations of 6 to 8 ppt. This illustrates the very short atmospheric lifetime of C₂HCl₃ and also why C₂HCl₃ itself is unlikely to impact stratospheric Cl levels.

2.2.8 Tetrachloroethene (C₂Cl₄)

C₂Cl₄ is mainly used for dry cleaning and as a metal degreasing solvent. Emissions of 580 kt estimated for 1984 by Class and Ballschmiter (1987) are significantly greater than global emissions derived from audited production figures for the years 1993 to 1996 of 261 Gg, 258 Gg, 278 Gg, and 289 Gg, respectively (Figure 2-1) (McCulloch and Midgley, 1996; updated by P.M. Midgley, M & D Consulting, Germany, private communication, 1998). There are no published results of long-term background measurements for C₂Cl₄, but comparison of recent results with data published in the early 1980s suggests that the atmospheric burden has measurably decreased during the last decade (Koppmann *et al.*, 1993; Wang *et al.*, 1995).

McCulloch and Midgley (1996; updated by P.M. Midgley, M & D Consulting, Germany, private communication, 1998) calculate that in the last few years SH usage has increased. However, 93% of 1995 industrial C₂Cl₄ usage was still in the NH. Thus, remote C₂Cl₄ concentrations are substantially higher in the NH (Atlas *et al.*, 1993; Koppmann *et al.*, 1993; Weidmann *et al.*, 1994; Wang *et al.*, 1995; Elkins *et al.*, 1996). The main C₂Cl₄ removal process is reaction with OH. Its atmospheric lifetime, assuming an average OH

concentration of $9.7 \times 10^5 \text{ cm}^{-3}$, is approximately 3 to 4 months (Table 2-4). Wang *et al.* (1995), Yokouchi *et al.* (1996), and Elkins *et al.* (1996) report significant seasonal variations in surface-level background concentrations. Blake *et al.* (1997) discuss seasonal differences in the C_2Cl_4 vertical distribution. The current background-surface NH mixing ratio varies from about 15 ppt in winter to 5 ppt during summer. Samples collected at Cape Grim, Tasmania, exhibit seasonality 6 months out of phase with the NH, with concentrations ranging from about 1.5 to 0.7 ppt (Elkins *et al.*, 1996). Kindler *et al.* (1995) estimate stratospheric loss of C_2Cl_4 at approximately 1% of its anthropogenic emissions.

2.2.9 Phosgene (COCl_2)

COCl_2 , which is not directly anthropogenically emitted to the troposphere, is a product of the breakdown of C_2HCl_3 , C_2Cl_4 , CHCl_3 , and CH_3CCl_3 . Its atmospheric mixing ratio is in the range of 10 to 60 ppt, with an average of about 20 ppt. The main removal process is wet deposition. Kindler *et al.* (1995) estimate a lifetime of 70 days, mostly due to hydrolysis in cloud water. These authors also estimate that COCl_2 transports about 10% as much Cl to the stratosphere as did CH_3CCl_3 when its NH concentration was approximately 150 ppt.

2.2.10 Other Chlorocarbons

There are isolated reports of measurement of other chlorocarbons in the atmosphere. Dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$) was reported by Class and Ballschmiter (1987) in Atlantic air at concentrations of 10 to 30 ppt. Dichloroethane has a lifetime of about 1 month and an estimated global flux of about 0.7 Tg yr^{-1} (Khalil, 1998). Tetrachloroethane ($\text{C}_2\text{H}_2\text{Cl}_4$), hexachlorobutadiene (C_4Cl_6), and vinylidene chloride ($\text{C}_2\text{H}_2\text{Cl}_2$) have all been observed at sub-ppt levels in marine or Arctic air (Class and Ballschmiter, 1986a,b, 1987; Atlas *et al.*, 1993; Yokouchi *et al.*, 1996). All are believed to be of anthropogenic origin. The mixed chlorobromomethanes are described elsewhere (Section 2.3.2).

2.2.11 Contributions to the Total Cl Budget

Although the longer-lived gases are generally the ones that come to mind when we think of stratospheric ozone depletion, collectively, the “other halocarbons” play a significant role. In 1998 CH_3Cl , at a mixing ratio of $550 \pm 30 \text{ ppt}$, is the most abundant chlorocarbon in

the atmosphere. Using measured tropical upper troposphere mixing ratios for CH_2Cl_2 ($15 \text{ ppt} \times 2 \text{ Cl molec.}^{-1}$) and CHCl_3 ($3 \text{ ppt} \times 3 \text{ Cl molec.}^{-1}$), C_2Cl_4 ($5 \text{ ppt} \times 4 \text{ Cl molec.}^{-1}$) estimated from a comparison of industrial source strength and lifetime with CH_2Cl_2 , and COCl_2 ($20 \text{ ppt} \times 2 \text{ Cl molec.}^{-1}$) estimated for the lower stratosphere, these gases deliver $100 \pm 20 \text{ ppt Cl}$ to the stratosphere. Thus, the complete inventory of “other halocarbons” contributes approximately $650 \pm 50 \text{ ppt Cl}$ to the stratosphere (or about 20% of the total organic Cl as reported in Chapter 1, Table 1-2).

2.3 BROMINATED COMPOUNDS

2.3.1 Methyl Bromide (CH_3Br)

Atmospheric CH_3Br is derived from both natural and anthropogenic sources. Once in the atmosphere, it is removed by atmospheric, terrestrial, and oceanic processes. Our understanding of the sources and sinks of this gas has improved since publication of the 1994 Assessment (Chapter 10 in WMO, 1995), but the overall picture is not yet resolved. A current summary of the estimated source and sink strengths is given in Table 2-5. The lifetime of CH_3Br in the atmosphere is shorter than that given in the 1994 Assessment, owing to the inclusion of new findings about its sinks. Uncertainties in the magnitude of specific processes have been reduced and new sinks have been identified since the 1994 Assessment. Nevertheless, uncertainties in our estimates of specific sources and sinks are still large. Based on our current understanding, the budget remains out of balance.

2.3.1.1 DISTRIBUTION AND TRENDS

Measurements of the spatial distribution and trends of CH_3Br place important constraints on the distribution and magnitude of its sources and sinks. An analysis of the implications of these constraints would be best carried out by sensitivity studies in a global model that can accurately represent its short lifetime and the inhomogeneity of its sources and sinks. Although some initial efforts have been carried out in this area with three-dimensional (3-D) models (e.g., Lee *et al.*, 1998) no complete modeling study exists that incorporates all the existing constraints. This is a reflection of the increasing complexity of the processes controlling CH_3Br . We review in this section the state of CH_3Br measurements

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Table 2-5. Summary of the estimated source and sink strengths of CH₃Br (Gg yr⁻¹).

Source or Sink Type	Source or Sink Best Estimate (Gg yr ⁻¹)	Source or Sink Range (Gg yr ⁻¹)
<u>Sources</u>		
Fumigation ^a - soils ^b	26.5	16 to 48
Fumigation ^a - durables ^c	6.6	4.8 to 8.4
Fumigation ^a - perishables ^d	5.7	5.4 to 6.0
Fumigation ^a - structure ^e	2	2 to 2
Gasoline ^f	5	0 to 10
Ocean ^g	56	5 to 130 ^h
Biomass burning ⁱ	20	10 to 40
<i>Subtotal</i>	<i>122</i>	<i>43 to 244</i>
<u>Sinks</u>		
Ocean ^g	-77	-133 to -37 ^h
Reactions (OH and hv)	-86	-107 to -65
Soils ^j	-42	-214 to -10
<i>Subtotal</i>	<i>-205</i>	<i>-454 to -112^h</i>
TOTAL	-83	-315 to 36^h

^a Based on 1992 production data (MBGC, 1994).

^b Assumes a mean 50% emission factor. Individual studies (Chapter 10 in WMO, 1995) indicate a range of 30 to 90% for the emission factors. These extremes have been adopted for the global uncertainty.

^c Assumes 51 to 88% emission factor.

^d Assumes 85 to 95% emission factor.

^e Assumes 100% emission factor.

^f Based on Chen *et al.* (1998), Baker *et al.* (1998a), and Hao (1986). These estimates are for emissions today, although in the past, when use of leaded gasoline was predominant in global consumption, this value could have been much higher (Thomas *et al.*, 1997).

^g The ocean uptake is from Yvon-Lewis and Butler (1997); low and high estimates are obtained by considering the full possible range in the physical parameters utilized in the uptake calculation (Yvon and Butler, 1996). The ocean source and range is obtained from:

$$\text{Source} = \text{Net Flux} - \text{Sink}$$

where Net Flux = -21 (-3 to -32) Gg yr⁻¹ (Lobert *et al.*, 1997; Groszko and Moore, 1998).

^h This table is constructed to demonstrate the balance or imbalance in the CH₃Br budget, yet also to keep all sources and sinks separate. The ocean is both a source and a sink for CH₃Br and the numbers are arranged in the table in such a way as to obtain maximum and minimum values for the source and sink subtotals simply by adding columns. For determining the range for the total budget, there is a constraint that the oceanic net flux equals -21 (-3 to -32) Gg yr⁻¹, which is based upon measurements of the surface saturation of CH₃Br (e.g., Lobert *et al.*, 1995, 1996, 1997; Butler *et al.*, 1995; Moore and Webb, 1996; Groszko and Moore, 1998). Oceanic sources and sinks must always add up to a value within this range. Thus, it is not possible to combine a very large oceanic sink with a very small oceanic source in evaluating the budget. However, the range for the atmospheric lifetime is calculated (e.g., based upon sinks) by separately adding up all of the large values within the sink ranges and all of the small values within the sink ranges and dividing each total into the atmospheric burden which, for a tropospheric mean of 10 ppt, is 146 Gg. For sinks, this yields a possible lifetime range of 0.32 to 1.3 years.

ⁱ Andreae *et al.*, 1996; N.J. Blake *et al.*, 1996.

^j Full range encompasses data of Shorter *et al.* (1995) and Serca *et al.* (1998). The "best estimate" used here is that given in Shorter *et al.* (1995).

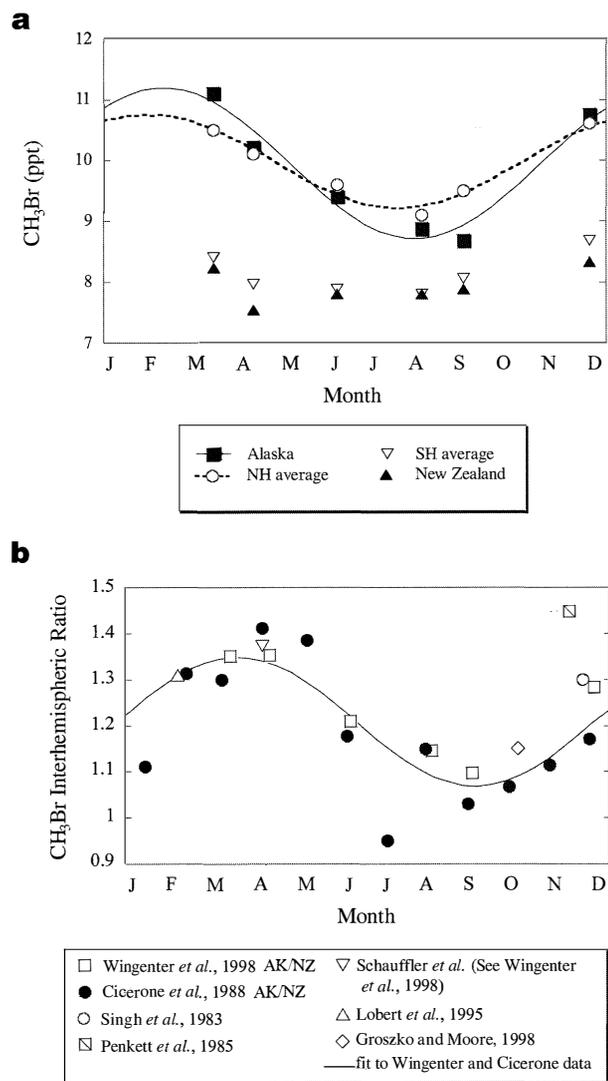


Figure 2-9. (a) Seasonal CH₃Br mole fractions in the NH, SH, Alaska, and New Zealand. (b) Seasonal variations in the CH₃Br interhemispheric ratio (NH/SH). The curve was fit to Cicerone *et al.* (1988) and Wingenter *et al.* (1998) data only, which are ratios of data from Alaska and New Zealand. Data points from Singh *et al.* (1983), Penkett *et al.* (1985), Lobert *et al.* (1995), Groszko and Moore (1998), and Schauffler *et al.* (as cited in Wingenter *et al.*, 1998) are ratios of estimated hemispheric averages.

that provide these constraints. Whenever possible, the implications of these measurements are discussed.

In recent years there has been a considerable increase in the number and scope of programs to measure the distribution and trends of atmospheric CH₃Br. The techniques being used are generally reporting comparable results (Lobert *et al.*, 1995a,b; 1996; Schauffler *et al.*, 1998a,b), but there remains a need for improved propagation and intercomparison of calibration standards so that the data can be combined for interpretive studies. Recent measurements and intercalibrations suggest that the current mean global, background tropospheric dry air mole-fraction of CH₃Br is between 9 and 10 ppt (Schauffler *et al.*, 1998a,b; Lobert *et al.*, 1995a,b; N.J. Blake *et al.*, 1996). From calculations that account for the vertical distribution of CH₃Br (e.g., Yvon and Butler, 1996), a tropospheric mixing ratio of 10 ppt corresponds to an atmospheric burden of 146 Gg.

The interhemispheric gradient of CH₃Br is of interest as a tool in diagnosing the geographical distribution of the sources and sinks of this compound. Because data from a range of different oceanic environments indicate that the oceans collectively constitute a net sink for tropospheric CH₃Br (see below), sources needed to balance the budget would need to be probably of terrestrial origin. The NH is thus expected to have higher mean concentrations than the SH, even without an anthropogenic component. To the extent that seasonal amplitudes and annual mean values apparently vary within each hemisphere (see below), these differences must be taken into account in quantifying the mean hemispheric abundances (Figure 2-9) (Wingenter *et al.*, 1998). The recent data generally support the 1994 Assessment (Chapter 10 in WMO, 1995) that the mean NH/SH surface concentration ratio is 1.3 ± 0.1 (Lobert *et al.*, 1995b, 1996; Groszko and Moore, 1998; Schauffler *et al.*, 1998b). In one study, consideration of the seasonal variability of CH₃Br yielded an equal-area, seasonally weighted average of 1.21 ± 0.03 (Wingenter *et al.*, 1998).

In the 1994 Assessment (WMO, 1995), only one study of the stratospheric vertical distribution of CH₃Br was available (Lal *et al.*, 1994), along with limited data on tropospheric vertical distributions that have now been published (D.R. Blake *et al.*, 1996; N.J. Blake *et al.*, 1996). Since then, a number of studies of stratospheric CH₃Br in the tropics, at midlatitudes, and at high latitudes

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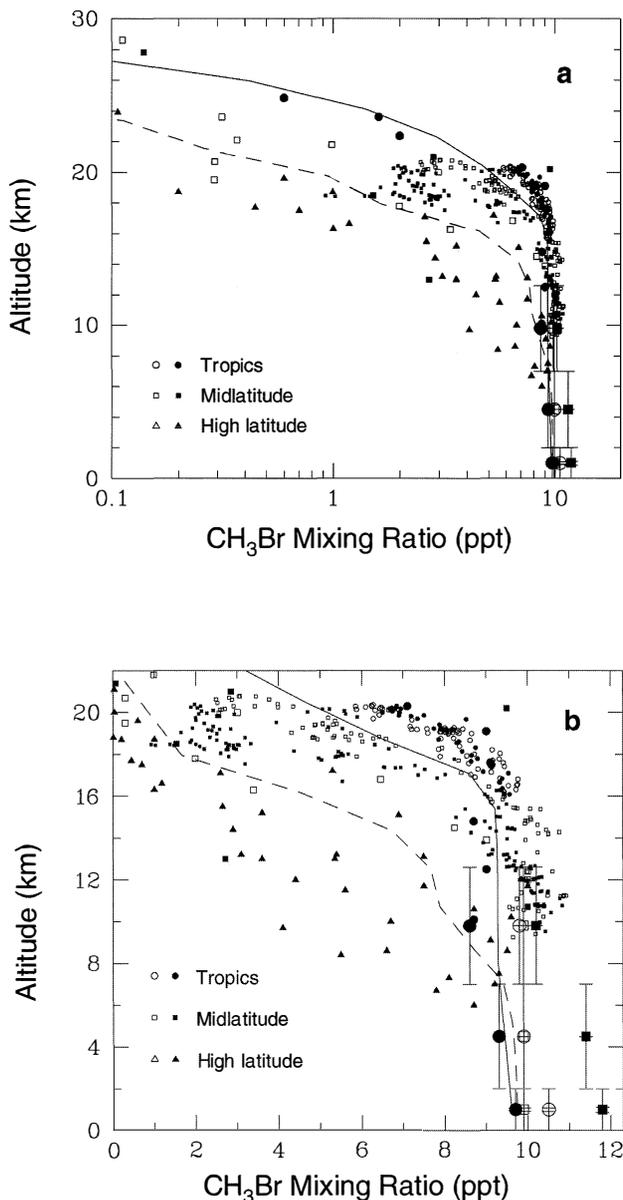


Figure 2-10. (a) Vertical profiles of CH₃Br measured at various latitudes during winter (filled symbols) and summer (open symbols) using different techniques (big symbols - Blake *et al.*, 1997; small symbols - Schauffler *et al.*, 1998a; medium symbols - Lal *et al.*, 1994, Kourtidis *et al.*, 1998). Some of the data are normalized to 10 ppt at the tropospheric level. Measurements are compared with the NASA Goddard Space Flight Center 2-D model (Jackman *et al.*, 1996) results; continuous line is for 15°N and dotted line is for 65°N. (b) Data shown on linear scale for greater clarity.

have been conducted (Figure 2-10). These studies together show tropospheric levels of CH₃Br penetrating vertically to as deep as 20 km in the tropics and as shallow as 10 km at high latitudes. Once in the stratosphere, CH₃Br decreases rapidly with height, suggesting that it is a significant source of free stratospheric Br. There is considerable variability of CH₃Br in the stratosphere, particularly around the Arctic vortex, where CH₃Br drops to below detection limits. Summertime vertical profiles in the tropical troposphere over the Atlantic Ocean do not appear to decline with increasing height, but during the winter, when flow from Asia is greatest and vertical convection is at a minimum, a vertical decrease of up to 1.5 ppt has been observed from the boundary layer to 10 to 12 km (Blake *et al.*, 1997). These same authors also show that the CH₃Br seasonal variations tend to decay in amplitude with increasing altitude in the troposphere. The midlatitude profiles in the lower stratosphere decrease faster in January than in July, presumably due to enhanced downward transport in the winter (Schauffler *et al.*, 1998b). Measurements of CH₃Br at the tropical tropopause in 1996 averaged 9.5 ± 0.4 ppt and represented 55% of the observed total organic Br (Schauffler *et al.*, 1998a).

The amplitude of the seasonal variation in tropospheric CH₃Br abundance appears to vary widely, even within the same hemisphere. Stations located at high northern latitudes tend to show the greatest seasonal variations in background CH₃Br (Wingenter *et al.*, 1998) of $\pm \sim 15\%$, which are roughly in phase with the variations in CH₃CCl₃ (Prinn *et al.*, 1995) and suggest the influence of OH seasonal variations. Such seasonal variations in CH₃Br at high NH latitudes (e.g., Pt. Barrow, Alaska; Mace Head, Ireland) are much larger than they are at SH midlatitudes (Cape Grim, Tasmania). This is not consistent with patterns observed for other gases, such as CH₃CCl₃ or C₂Cl₄, with mixing ratios controlled primarily by tropospheric OH and for which seasonal variations are roughly in phase at these sites (Prinn *et al.*, 1995). This suggests that factors in addition to tropospheric OH are involved in controlling variability of CH₃Br; these additional factors may be sources or sinks present in one or both hemispheres (Simmonds *et al.*, 1998b).

Although tropospheric vertical profiles (e.g., Blake *et al.*, 1997; Schauffler *et al.*, 1998a) (see Figure 2-11) can be used to place lower limits on the lifetimes of some gases, this may not be the case for CH₃Br. If the tropospheric chemical lifetime of a gas is short with

respect to vertical mixing in the free troposphere, and the gas is emitted primarily at the surface (i.e., the bottom of the troposphere), then one would expect to see lower amounts in the upper troposphere. However, once emitted, the tropospheric chemical lifetime of CH₃Br due to removal by OH is about 1.7 years. This lifetime is sufficiently long to prevent the development of a large negative vertical gradient. The only apparent lowering of CH₃Br is near the tropopause, where there is some exchange with the lower stratosphere. A positive or negative vertical gradient might be expected near the surface for a gas such as CH₃Br, which has potentially large surface sources or sinks in some regions. It is thus possible that temporary vertical gradients of CH₃Br could appear at some locations that represent primarily sources or primarily sinks, but this would depend heavily on local mixing and would not place a significant constraint on the large-scale atmospheric lifetime of this gas.

The search for temporal trends in tropospheric CH₃Br has received special attention during the past few years because of its importance with respect to assessing the magnitude of anthropogenic releases relative to the natural sources. Unfortunately, from this perspective the period of greatest interest is not the present, when anthropogenic releases are believed to be relatively constant (see below and Chapter 10 in WMO, 1995), but rather the decades of the 1960s through the 1980s, when agricultural fumigation and leaded gasoline usage were undergoing the greatest changes. The only time series measurements from the critical period are those of Khalil *et al.* (1993) dating from 1978 in the NH and from 1983 globally. These show a significant mean, latitudinally weighted global rate of increase of 0.15 ± 0.08 (90% confidence limit) ppt yr⁻¹ between 1983 and 1992. Available data are not sufficient at this point to determine the magnitude of CH₃Br trends since 1992.

2.3.1.2 ANTHROPOGENIC SOURCES OF ATMOSPHERIC CH₃Br

Automobile Emissions

Two estimates of CH₃Br emissions by automobiles were mentioned in the 1994 Assessment (WMO, 1995), one that represented emissions of 9 to 22 Gg yr⁻¹ and one that represented emissions of 0.5 to 1.5 Gg yr⁻¹. The high estimate was based upon a study by Baumann and Heumann (1989) and the low estimate was from unpublished calculations. Since then, Thomas *et al.*

(1997) estimated the global use of Br in gasoline since 1945, noting a peak production in 1970 of 160 Gg of Br, which subsequently has declined to near 30 Gg in 1995. This study suggested that CH₃Br emissions from leaded gasoline could have fallen from about 17 ± 5 to 7.6 ± 2 Gg yr⁻¹ between 1984 and 1992. Two other papers (Chen *et al.*, 1998; Baker *et al.*, 1998a), along with the findings of Hao (1986), suggest that global CH₃Br emissions from automobiles today probably are below 5 Gg yr⁻¹ (Table 2-5) and may be insignificant. Although there is still a large degree of uncertainty involved in making these estimates, none of the recent studies tends to support high emissions from automobiles today.

Fumigation

Emissions from the use of CH₃Br as a fumigant for durables, perishables, and structures historically have been considered to be a large fraction of the amount applied. Emissions from fumigation of soils, which represents the heaviest use of CH₃Br (approximately 80%), are more difficult to quantify. The 1994 Assessment noted that there was a wide range of possibilities for the fraction of CH₃Br emitted (Chapter 10 in WMO, 1995). Since then, a number of studies have shown that standard polyethylene tarps do little to retard the emission of CH₃Br to the atmosphere and provide little information to change the estimate of about 50% for globally averaged emissions to the boundary layer (Yagi *et al.*, 1995; Yates *et al.*, 1996a,b,c, 1997; Majewski *et al.*, 1995). Specific agricultural practices and processes could reduce emissions in the future. Wang *et al.* (1997a,b) have demonstrated the efficacy of high-barrier films in reducing CH₃Br emissions from fumigated soils, and Yates *et al.* (1998) noted that shallow injections could still be conducted with a low loss rate to the atmosphere (about 1%), if a high-barrier film (HBF) is used for a period of 10 to 15 days.

Removal of CH₃Br within soils following fumigation is likely both microbially mediated and abiotic (Miller *et al.*, 1997; Oremland *et al.*, 1994). It also has been suggested recently that CH₃Br can be removed from a plume originating from a fumigated field by interaction with soils during dispersal throughout the boundary layer (Woodrow *et al.*, 1997). However, not enough is known about the global impact of these effects to improve the estimates given in the 1994 WMO Assessment.

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Biomass Burning

Biomass burning was first suggested as a source for atmospheric CH_3Br by Manö and Andreae (1994). From a rather limited study, the authors reported a possible range of 10 to 50 Gg yr^{-1} for global emissions from this source. Although the mean of 30 Gg yr^{-1} was used in earlier estimates of this flux, it was later revised to 20 Gg yr^{-1} based upon additional studies of savanna fires by Andreae *et al.* (1996) and of savanna and Brazilian agricultural areas by N.J. Blake *et al.* (1996). The consistency of emissions and emission ratios for the various fires suggests a slightly narrower range for the global mean than that of Manö and Andreae (1994), perhaps 10 to 40 Gg yr^{-1} . The remaining uncertainty is to a large extent due to the scarcity of data from tropical forest burning, one of the largest sources of pyrogenic emissions. The few fires investigated showed highly diverse emission ratios and represent only a small fraction of the burning practices and deforestation regions.

2.3.1.3 SURFACE INTERACTIONS

Ocean

The ocean is both a source and a sink of CH_3Br . Observations of surface saturations and calculations of degradation rates indicate that CH_3Br is produced and destroyed simultaneously everywhere in the ocean. The complexities of the interactions between ocean and atmosphere require an understanding of ocean production, ocean consumption, and net flux. The relationships among these processes have been discussed by Butler (1994), Penkett *et al.* (Chapter 10 in WMO, 1995), and Butler and Rodríguez (1996). We summarize our understanding of the different processes, in particular how the magnitudes of sources and sinks are determined, with a view to evaluating their relative uncertainties. Details of the calculations and measurements supporting the current estimates are discussed.

The magnitude of the ocean uptake is determined by the atmosphere-to-ocean transfer of CH_3Br , followed by degradation in the ocean waters by chemical and biological processes. Given a parameterization of air-sea gas exchange, ocean uptake and degradation by inorganic processes can be calculated from a knowledge of the winds near the ocean surface, the sea surface temperature, and laboratory measurements of CH_3Br solubility, diffusivity, hydrolysis, and nucleophilic substitution in seawater. Uncertainties in diffusivity, solubility, and chemical degradation have been reduced

significantly since the 1994 Assessment (WMO, 1995) (DeBruyn and Saltzman 1997a,b; Jeffers and Wolfe 1996b; King and Saltzman, 1997). Based on chemical loss alone, Yvon and Butler (1996) estimated a partial ocean lifetime of 2.7 (2.4 to 6.5) years. This estimate is more constrained than the value of 3.7 (1.3 to 14) years for this partial lifetime used in the 1994 Assessment (Butler, 1994). The reduction in the uncertainty of the partial oceanic lifetime was achieved by taking into account the seasonal and spatial covariance among ocean surface and boundary layer parameters using a 2-D database of sea surface temperature, salinity, and surface wind speed, and assuming an interhemispheric ratio of 1.3 (Yvon and Butler, 1996). We must emphasize that the above estimates do not depend on the new measurements of super- or undersaturation discussed below, but only on the physical and chemical state of the ocean mixed layer and air-sea interface.

Shipboard measurements are used to obtain the net flux across the sea surface. A negative flux is deduced from an undersaturation of the surface waters, indicating that the ocean uptake is larger than ocean emission of CH_3Br . Knowledge of the physical and chemical conditions at a specific location enables calculation of the expected ocean undersaturation, in the absence of biological processes. However two measurement campaigns in the Labrador Sea (Moore and Webb, 1996) and the Southern Ocean (Lobert *et al.*, 1997) showed that the cold high-latitude waters in both hemispheres were significantly more undersaturated than expected. Because chemical removal is slow in the cold waters, some other process must be removing CH_3Br in order to sustain the observed undersaturations (-35%). Work by King and Saltzman (1997) showed that bacteria in warmer waters could remove CH_3Br at almost twice the rate of chemical processes alone. Biological degradation of aquatic CH_3Br in fresh water and in salt water also has been found by Goodwin *et al.* (1997) and Connell *et al.* (1997). Yvon-Lewis and Butler (1997) used the recent in situ measurements and biological degradation data to update their estimate of the ocean uptake to -77 Gg yr^{-1} , yielding a partial lifetime of atmospheric CH_3Br with respect to oceanic loss of 1.9 (1.1 to 3.9) years due to both chemical and biological degradation. Thus, their assessment of biological degradation to a global scale reduces the estimated partial lifetime due to oceanic removal by 30%.

As discussed by Butler (1994), by Butler and Rodríguez (1996), and in Chapter 10 of WMO (1995),

the ocean uptake discussed above (which determines the partial ocean lifetime) is not the same as the globally extrapolated net flux across the ocean surface. The latter determines whether the ocean is a net source or sink of CH₃Br to the troposphere. Since the 1994 Assessment (WMO, 1995), which stated that the ocean was a net source of atmospheric CH₃Br, studies in the Pacific (Lobert *et al.*, 1995b; Groszko and Moore, 1998), the Atlantic (Butler *et al.*, 1995; Lobert *et al.*, 1996), the Labrador Sea (Moore and Webb, 1996), and the Southern Ocean (Lobert *et al.*, 1997) showed that much of the ocean was a net sink for atmospheric CH₃Br. These studies tighten constraints upon the estimate of the global net flux of CH₃Br. The latest estimates indicate that the ocean today is a net sink for atmospheric CH₃Br. Lobert *et al.* (1997) derived a net flux of -21 (-11 to -32) Gg yr⁻¹ from data collected on two extensive cruises and one regional cruise; Groszko and Moore (1998) derived a net flux of -10 (-3 to -13) Gg yr⁻¹ with data combined from one extensive and one regional expedition. The uncertainties quoted arise from uncertainties in the physical parameters used in the derivation of ocean uptake for regions sampled. Uncertainties due to extrapolation of measurements to the global ocean are more difficult to quantify, and this should be kept in mind in assessing the uncertainties in the CH₃Br budget. However, changes in this net flux are separate from the estimated partial oceanic lifetime. Because the Lobert *et al.* (1997) estimate includes data that are based upon broader spatial and temporal coverage than those of Groszko and Moore (1998), we have kept the “best estimate” of -21 Gg yr⁻¹ given by Lobert *et al.* (1997) for budget and lifetime calculations in Table 2-5 (footnote h), but have extended the possible range to include that given by Groszko and Moore (1998). These extrapolations are based primarily on sampling of diverse regions of the oceans (i.e., coastal upwelling, equatorial, high latitude) and do not assume any correlation with indicators of biological activity.

Two models using apparent correlations of productivity with temperature and chlorophyll indicated that there might be a net source of atmospheric CH₃Br in sub-polar and polar waters and that this source could outweigh the sink in the remainder of the ocean (Anbar *et al.*, 1996; Pilinis *et al.*, 1996). However, the measurements in the cold waters of the Labrador Sea and the Southern Ocean indicated that these regions were also a net sink during a time of year when they were expected to be a net source. From these studies, it is

clear that one cannot depend upon a simple relationship between CH₃Br and chlorophyll or temperature for predicting net CH₃Br production or net CH₃Br fluxes from the ocean. Recently, Baker *et al.* (1998b) found a seasonal cycle in the saturation of CH₃Br in the coastal waters of the North Sea, with supersaturation occurring between June and September, when a particular type of phytoplankton was present (see below), and undersaturation for the rest of the year. Furthermore Baker *et al.* (1998b) also observed the northeast Atlantic open ocean to be supersaturated during a cruise in September, when there was again evidence for the presence of these phytoplankton. This confirms that the relationship between CH₃Br and chlorophyll is not simple but also depends on the type of species present, which are both spatially and temporally variable. Further studies of this seasonal behavior are needed to place additional constraints on global estimates of the net flux.

Given the oceanic net CH₃Br flux of -21 Gg yr⁻¹ (extrapolated from measurements, with a possible range of -3 to -32 Gg yr⁻¹) (Lobert *et al.*, 1997) and the calculated oceanic uptake of -77 Gg yr⁻¹ (with an estimated range of -37 to -133 Gg yr⁻¹) (Yvon-Lewis and Butler, 1997), emission from the ocean is estimated at 56 Gg yr⁻¹ (with an estimated range of 5 to 130 Gg yr⁻¹). We emphasize that the ocean source and its uncertainty range are calculated from the net flux and ocean sink. Oceanic sources and sinks must always add up to a value within the -3 to -32 Gg yr⁻¹ range currently estimated for the net ocean flux. Thus, it is not possible to combine a very large oceanic source with a very small oceanic sink in evaluating the budget.

Until recently, little information on the production of CH₃Br by marine organisms was available. Scarratt and Moore (1996) and Saemundsdóttir and Matrai (1998) have found in laboratory studies that numerous species of marine phytoplankton produce CH₃Br, at rates that vary by almost a factor of 20 (1.7 to 30 picograms CH₃Br per day per microgram of chlorophyll *a*). However, only the highest observed rates of production by these organisms begin to support observed field concentrations. Baker *et al.* (1998b) have observed CH₃Br concentrations in the North Sea, a coastal environment, to be higher when the spring and summer bloom of phytoplankton is dominated by the prymnesiophyte *Phaeocystis*. Coastal waters are often supersaturated in CH₃Br (e.g., Lobert *et al.*, 1995b, 1996; Butler *et al.*, 1995; Sturges *et al.*, 1993). Baker *et al.* (1998b) also observed, in the open ocean of the northeast Atlantic, a strong correlation between

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CH₃Br and the pigment hexanoyloxyfucoxanthin, which indicates the presence of prymnesiophytes.

In summary, data from five field investigations suggest that the oceans as a whole can be considered as a net sink for atmospheric CH₃Br, sustained by a balance between aquatic production and degradation. As noted by Anbar *et al.* (1996), changes in water temperature, and, for that matter, anything affecting the community composition of marine organisms, could alter this picture. Production by phytoplankton and degradation by bacteria have been observed, but this does not rule out the possibility of production by bacteria or production or degradation by zooplankton. There even may be some degradation by certain species of phytoplankton.

Soils

Whereas microbial losses in the soil during fumigation can be thought of as reducing a source of CH₃Br, the loss of ambient levels of CH₃Br to soils must be treated as a global sink and built in to computations of the CH₃Br atmospheric lifetime. The study of Shorter *et al.* (1995) estimated a partial lifetime of 3.4 years for soil uptake of CH₃Br. This study was not included in the 1994 Assessment (WMO, 1995), and the calculated lifetime of atmospheric CH₃Br (1.3 years) included only oceanic and atmospheric sinks. With the addition of the Shorter *et al.* (1995) results, this calculation yielded an atmospheric lifetime of 0.8 yr (0.7 yr, now, with the biological oceanic sink included). Unfortunately, the large uncertainties of the Shorter *et al.* (1995) estimate ($42 \pm 32 \text{ Gg yr}^{-1}$) make this a difficult sink to quantify with much confidence. Additional studies are needed to narrow this range.

Serca *et al.* (1998) have carried out measurements similar to those of Shorter *et al.* (1995). Although the deposition velocities measured are of a similar magnitude, they estimate an even larger global soil sink of $143.4 \pm 70.2 \text{ Gg yr}^{-1}$. The higher estimate is primarily due to their using a different global inventory for soil types. With an atmospheric abundance of 146 Gg, such values would reduce the estimated partial lifetime of CH₃Br due to soil uptake to 1.0 (0.7 to 2.0) years, but adoption of such large soil uptake rates would increase even further the imbalance between sources and sinks. Other findings by Miller *et al.* (1997) and Woodrow *et al.* (1997), both done mainly with regard to fumigation levels, also qualitatively support the presence of a natural soil sink for atmospheric CH₃Br.

Plants

No solid evidence of a plant sink for CH₃Br was presented in the 1994 Assessment (Chapter 10 in WMO, 1995). Recently, however, Jeffers and Wolfe (1996a, 1998) have shown that leaves, roots, and stems of many plants remove CH₃Br from air. The measurements were made on plant parts in enclosed, 20-ml vials at predominantly nmol mol⁻¹ to μmol mol⁻¹ (parts per billion-parts per million (ppb-ppm)) levels of CH₃Br, but the observed loss rates, ranging from 0.96 to 150 h⁻¹ cm⁻², were linear with concentration. Current calculations suggest that these rates, applied to the global atmosphere, may be small relative to the atmospheric, oceanic, and soil sinks. Additional studies conducted at ambient levels of CH₃Br with whole plants and plants in natural systems are needed.

The possibility of plants being a source of atmospheric CH₃Br exists, but no published studies to date have focused on CH₃Br fluxes from plants at ambient levels. Some studies have shown that methyl iodide (CH₃I) is emitted at high rates from rice plants (Muramatsu and Yoshida, 1995) and others have shown that CH₃Br, CH₃I, and CH₃Cl are emitted from the leaf disks of many plants (e.g., Saini *et al.*, 1995).

2.3.1.4 ATMOSPHERIC SINKS

The one significant change in our estimate of the magnitude of this dominant removal process since the 1994 Assessment (WMO, 1995) is the recomputation of the mean tropospheric amount of OH, owing to a change in the AGAGE calibration scale for CH₃CCl₃ (Prinn *et al.*, 1995). This effectively raised the estimated mean concentration of tropospheric OH by about 15%, which correspondingly increased the calculated removal rate of CH₃Br by in situ atmospheric reaction and decreased the calculated CH₃Br atmospheric lifetime. The best estimate for the partial lifetime of atmospheric CH₃Br with respect to in situ reactions is now 1.7 years (±25%) (Yvon-Lewis and Butler, 1997). No new information has evolved regarding photolytic loss of CH₃Br, which remains small with a lifetime on the order of 35 years.

We note that the calculation of the atmospheric lifetime of CH₃Br is carried out by global two-dimensional models that assume that the CH₃Br distribution is uniform enough that the scaling of lifetimes with that of CH₃CCl₃ (Prinn *et al.*, 1995) is a good approximation. Because recent studies have

suggested a shorter lifetime for CH₃Br than given in the 1994 Assessment (WMO, 1995), this assumption should be reconsidered to determine whether use of three-dimensional models is required.

2.3.1.5 SUMMARY BUDGET, LIFETIME, AND OZONE DEPLETION POTENTIALS (ODPs)

Because the observed growth rate of atmospheric CH₃Br has been near zero in recent years, a balanced budget requires that the source and sink strengths are equal. However, current best estimates for those sources and sinks that have been studied differ, with the sinks being 83 Gg yr⁻¹ larger than the sources (Table 2-5)¹. There are still large uncertainties in the estimates of the individual flux strengths, which allow the possibility of a balanced budget. In particular uncertainties exist in the net flux across the ocean surface and even more in the estimated soil sink, because both of these are extrapolated from measurements at specific sites. It is pertinent to ask what changes in ocean and soil sink estimates would be necessary to balance the CH₃Br budget. Examination of Table 2-5 indicates that one way to achieve such a balance would require both negligible soil sinks and a change in the estimated ocean net flux from -21 Gg yr⁻¹ to +20 Gg yr⁻¹. Although regions of ocean supersaturation have been observed in various ocean cruises, it is difficult to envision an unsampled ocean "hot spot" of CH₃Br production that would change the global flux estimates by this amount. At the same time, several studies have found evidence of soil sinks, and again it is unreasonable to completely neglect them.

Thus, the data given in Table 2-5 suggest that there is an unaccounted source of atmospheric CH₃Br. Similar inconsistencies between the sources, sinks, and global atmospheric burden of CH₃Cl are discussed in Section 2.2.4. The relationship between these two compounds has not been sufficiently studied.

The current best estimate of the lifetime of atmospheric CH₃Br is 0.7 years and, considering uncertainties in the estimates of the individual sink processes, ranges from 0.32 to 1.3 years (Table 2-5, footnote h). It should be noted that the lowest value in

this range would require sources far in excess of (i.e., 310 Gg yr⁻¹ greater than) current estimates (Table 2-5). If current estimates for CH₃Br sources in Table 2-5, together with the global atmospheric burden, were used to estimate the atmospheric lifetime, we would obtain a value of 1.2 (0.8 to 3.0) years. A recent study (Colman *et al.*, 1998) has compared the variance of CH₃Br measurements taken from aircraft to those of CH₃Cl and other species. Utilizing a relationship between variance and atmospheric residence time first proposed by Junge (1963), these investigators have estimated a lifetime of about 0.7 to 0.8 years, consistent with the estimates utilizing the sinks in Table 2-5.

The values in Table 2-5 indicate that roughly 50% of the accounted CH₃Br sources arise from anthropogenic activity (defined as both fumigation and biomass burning). Specifically, about 30% of the accounted CH₃Br sources are due to fumigation. On the other hand, the magnitude of the total anthropogenic sources is 30% of the magnitude of the total estimated sinks, with fumigation practices being 20%. Consideration of the uncertainties in the CH₃Br budget introduces uncertainties of at least a factor of 2 in the above fractions.

The steady-state Ozone Depletion Potential (ODP) of CH₃Br was discussed in the previous 1994 Assessment (Chapter 10 in WMO, 1995). An approximate expression for the steady-state ODP is given by (Solomon and Albritton, 1992):

$$\text{ODP}_{\text{CH}_3\text{Br}} \approx \left[\frac{1}{3} \frac{\text{MW}_{\text{CFC-11}} \tau_{\text{CH}_3\text{Br}}}{\text{MW}_{\text{CH}_3\text{Br}} \tau_{\text{CFC-11}}} \beta \right] \left[\left\langle \frac{F_{\text{CH}_3\text{Br}}(z)}{F_{\text{CFC-11}}(z)} \alpha \right\rangle \right]$$

$$\text{ODP}_{\text{CH}_3\text{Br}} \approx [\text{BLP}] [\text{BEF}] \quad (2-1)$$

where MW_{CH₃Br} and MW_{CFC-11} denote the molecular weights of CH₃Br and CFC-11, respectively; F_{CH₃Br}(z)/F_{CFC-11}(z) represents the Br release from CH₃Br relative to the Cl release from CFC-11 in the stratosphere; α denotes the efficiency of the released Br in catalytic removal of ozone, relative to Cl; β is the decrease in the mixing ratio of CH₃Br at the tropical tropopause, relative to the mixing ratio at the Earth's surface; < > denotes

¹ The ranges in the values given in Tables 2-5 and 2-6 should not be interpreted as indicating a probability distribution of the parameters discussed, since the methodology used in deriving some of these ranges is not amenable to a statistical interpretation. For example, there are only a few studies of the percent of soil fumigation released to the boundary layer, or of the soil sink, and the maxima and minima of available estimates have been adopted.

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spatial averaging of the quantity with the appropriate weighting; and 1/3 is the ratio of the number of halogen atoms in CH₃Br relative to those in CFC-11. The time constants $\tau_{\text{CFC-11}}$ and $\tau_{\text{CH}_3\text{Br}}$, relating the change in atmosphere burden to a change in emissions at steady state, are equal to the total atmospheric lifetimes. The terms in brackets are the so-called Bromine Loading Potential (BLP) and Bromine Efficiency Factor (BEF). The value of the BLP depends on tropospheric surface removal processes, whereas the value of the BEF is determined by the chemistry of CH₃Br and inorganic Cl in the stratosphere.

Evaluation of the BEF requires use of a model incorporating both stratospheric transport and chemistry. Changes in recommended reaction rates for Br species have been documented in the latest NASA/Jet Propulsion Laboratory (JPL) review (DeMore *et al.*, 1997). Inclusion of the new recommended rates in 2-D models has increased the calculated BEF from a recommended value of 48 in the 1994 Assessment (WMO, 1995) to 58 in this Assessment (Ko *et al.*, 1998; Wuebbles *et al.*, 1998). These changes arise mostly from incorporation of fast hydrolysis rates for BrONO₂ in sulfate aerosols, and new absorption cross sections for hypobromous acid (HOBr).

The 1994 Assessment considered uncertainties in stratospheric Br partitioning due to possible production of hydrogen bromide (HBr) from reaction of bromine monoxide (BrO) with hydroperoxyl radicals (HO₂). Two groups have recently reported observations of stratospheric HBr using far infrared emission. Johnson *et al.* (1995) derived an average HBr mixing ratio of 2.8 ± 0.8 ppt in the altitude range 22 to 34 km based on seven balloon flights between 1988 and 1994 around 34°N. Carlotti *et al.* (1995) reported HBr observations of 1.15 ± 0.46 ppt between 20 and 36.5 km at 34°N in May 1993. Nolt *et al.* (1997) reported measurements from May 1994 showing an average HBr mixing ratio of 1.31 ± 0.39 ppt between 20 and 36.5 km. These observations of about 1 to 2 ppt of HBr are larger than model predictions that consider HBr production due only to reactions of Br with HO₂ and formaldehyde.

The HBr observations have prompted suggestions that the reaction between BrO and HO₂ may have a minor channel producing HBr. Larichev *et al.* (1995) reported an upper limit for this channel of 1.5% from the non-observation of ozone as a product of this reaction,

whereas Mellouki *et al.* (1994) studied the reverse reaction and predicted that the upper limit for the yield is in fact less than 0.01%. A branching ratio of 0.6% would be required to match the observations, according to the model study of Ko *et al.* (1998). Chipperfield *et al.* (1997) and Chartrand and McConnell (1998) have considered whether an HBr production channel in the reaction between BrO + OH could resolve the HBr discrepancy. The only reported study of this reaction is by Bogan *et al.* (1996), who did not measure the reaction branching ratio. A branching ratio of 1.3% would be required to match the measured HBr from the balloon studies (Ko *et al.*, 1998).

Using a lifetime of 0.7 years and a value of 58 for the BEF, a steady-state ODP of 0.4 is calculated. Equation (2-1) is also useful to determine the impact of uncertainties in various parameters on the calculated ODP. Table 2-6 shows the range of ODP values resulting from our incomplete knowledge of various parameters.

2.3.2 Other Brominated Compounds

The abundance and composition of organic Br in the troposphere can be quite variable. In contrast to the more stable halons or CH₃Br, there are a number of organic Br compounds that exhibit a large range in concentration and have a significant impact on the budget of atmospheric Br. The presence of a pool of reactive organic Br species may lead to significant effects on atmospheric oxidation processes. For example, there has been compelling evidence of significant tropospheric ozone depletion in the Arctic marine boundary layer due to reactive Br chemistry, and organic Br precursors have been suggested as the source of reactive Br (Barrie *et al.*, 1988; Hausmann and Platt, 1994). In the stratosphere, the impact of reactive Br on catalytic ozone loss has been examined and found to be significant, but the role of short-lived organic Br in the upper troposphere and lower stratosphere is not yet well defined (see Ko *et al.*, 1997).

In addition to CH₃Br and halons, the major compounds that contribute to total organic Br in the atmosphere are dibromomethane (CH₂Br₂), bromoform (CHBr₃), mixed bromochloromethanes (CH₂BrCl, CHBrCl₂, CHBr₂Cl), and ethylene dibromide (C₂H₄Br₂). Minor amounts of ethyl bromide (C₂H₅Br) and halothane (CF₃CHBrCl) have also been reported, but these are not considered here.

2.3.2.1 MEASUREMENTS, DISTRIBUTIONS, AND TRENDS

Surface Measurements

Measurements of shorter-lived organic Br compounds (i.e., organic Br compounds other than CH₃Br and the halons) in the atmosphere have been made on samples from a number of surface sites (Table 2-7). These sites have been concentrated either in polar regions or in marine and coastal areas. Because of different analytical techniques applied, few studies report simultaneous measurements of all the organic Br species relevant to this discussion. Still, a reasonably consistent picture of the atmospheric concentrations of different organic Br compounds can be obtained from the existing dataset. From these data, the relative abundance of

shorter-lived organic Br species in the boundary layer is typically CHBr₃ > CH₂Br₂ > CHBr₂Cl ≈ CHBrCl₂ ≈ CH₂BrCl > C₂H₄Br₂, though it should be kept in mind that these measurements are often made near biogenic source regions. Average values of 5 to 10 ppt (as Br) from these gases correspond to 30 to 50% of the Br contribution from CH₃Br and the halons. There are no published data on ambient levels of these trace gases in urban or midcontinental regions.

Latitudinal surveys have shown increased levels of shorter-lived organic Br compounds over biologically productive marine waters. Both coastal and equatorial upwelling areas are associated with the highest levels of reactive organic Br. Typically, strong correlations are observed between atmospheric concentrations of CHBr₃,

Table 2-6. Summary of the range in the calculated steady-state ODP for CH₃Br. Each row illustrates the impact of uncertainties in a given parameter by keeping other parameters fixed to their best estimates and by using Equation (2-1) to propagate the uncertainty in the parameter examined. We have assumed a value of 1.0 for β (the decrease in the mixing ratio of CH₃Br at the tropical tropopause, relative to the mixing ratio at the Earth's surface).

Parameter	Value	Range	$\tau_{\text{CH}_3\text{Br}}$	BLP	BEF ^a	ODP
$\tau_{\text{atmos}}^{\text{b}}$ (yrs)	1.7 ± 25%	1.3 to 2.1	0.62 to 0.77	0.0060 to 0.0073	58	0.35 to 0.42
$\tau_{\text{ocean}}^{\text{c}}$ (yrs)	1.9	1.1 to 3.9	0.56 to 0.88	0.0053 to 0.0083	58	0.31 to 0.48
$\tau_{\text{soil}}^{\text{d}}$ (yrs)	3.4	6.8 to 14.6	0.39 to 0.84	0.0037 to 0.0080	58	0.22 to 0.46
$\tau_{\text{CFC-11}}^{\text{e}}$ (yrs)	50 ± 10%	55 to 45	0.71	0.0061 to 0.0075	58	0.35 to 0.44
$F_{\text{CH}_3\text{Br}}/F_{\text{CFC-11}}^{\text{f}}$	1.12 ± 5%	0.92 to 1.24	0.71	0.0067	49.2 to 66.6	0.33 to 0.45
Branching ratio of 0.006 for BrO + HO ₂ → HBr + O ₃			0.71	0.0067	52	0.35
Branching ratio of 0.013 for BrO + OH → HBr + O ₂			0.71	0.0067	56	0.37

^a We have used a bromine efficiency factor (BEF) of 58 as presented by Ko *et al.* (1998). This is derived from the AER 2-D model and was calculated using the DeMore *et al.* (1997) recommendations. Other models may give different values. We note that, in general, the model-calculated BEF is a convolution of the ratio of F factors and α, and the expression in Equation (2-1) is only approximate. Equation (2-1) is used to estimate the uncertainty in BEF induced by the uncertainty in the ratio of F factors derived from observations.

^b An overall ±25% uncertainty is assumed based on ±10% uncertainty in the reaction rate with OH (DeMore *et al.*, 1997), a ±20% uncertainty in the scaling with the CH₃CCl₃ lifetime, and a ±30% uncertainty in the stratospheric loss rate.

^c Lifetime and range as quoted in Yvon-Lewis and Butler (1997).

^d Shorter *et al.*, 1995; Serca *et al.*, 1998.

^e Chapter 5 in Kaye *et al.*, 1994.

^f Schauffler *et al.*, 1998b.

SHORT-LIVED COMPOUNDS

Table 2-7. Measurements of short-lived (reactive) organic Br compounds in the atmosphere. Concentrations are given in ppt.

Location	Concentration (ppt)						Ref.
	CH ₂ Br ₂	CH ₂ BrCl	CHBrCl ₂	CHBr ₂ Cl	CHBr ₃	C ₂ H ₄ Br ₂	
<u>Continental/Coastal (Surface)</u>							
Alert, NWT, 82°N				0.13	1.7	0.2	4,5
Alert, NWT, 82°N, before polar sunrise	0.8			0.3	2.6		8
Alert, NWT, 82°N, after polar sunrise	0.8	0.22	0.26	0.2	1.6		8
Alert, NWT, 82°N, winter		0.15		0.3	3.0		9
Alert, NWT, 82°N, summer		0.14		0.14	0.84		9
Spitzbergen, 79°N	0.45		0.12	0.33	0.45		11
Barrow, AK, 71°N	1.9	0.5	0.6	0.3	2.3	0.1	17
Barrow, AK, 71°N					≈6		12*
<u>Marine/Coastal (Surface)</u>							
Pacific, 19°N, Hawaii					≈3		12*
Pacific, 19°N, Hawaii				0.25	3.4	0.4	4
Pacific, 10°S to 15°N	1.8			0.24	1.8		3
Pacific, 30 to 40°N				0.17	0.89		4
W. Pacific, 40°S to 40°N	0.87				1.04		7
W. Pacific, 40°S to 40°N	0.59				0.63		7
Tropical Pacific (< 500 m)	1.01		0.16	0.17	1.55		16
SE Asia, marine, 0 to 30°N	0.77				1.2		7
N. Atlantic	2.7				0.85		13
NE Atlantic	3.4		0.6	0.5	6.6		10
S. Atlantic	1.6				0.88		13
SE Atlantic	1.2		0.4	0.3	1		10
Antarctic, 64°S	3.7		3.8		6.3		6
<u>Free Troposphere</u>							
Mauna Loa, HI, 3.4 km				0.13	0.20	0.06	4
Mauna Loa, HI, 3.4 km:							
Autumn	0.78	0.13	0.19	0.10	0.33		14
Winter	0.86	0.18	0.21	0.14	0.61		14
Spring	0.86	0.20	0.21	0.10	0.30		14
Summer	0.67	0.14	0.15	0.07	0.22		14
Atlantic, above inversion	1.2		0.2	0.1	0.6		10
Tropical tropopause	0.5 - 0.72	0.12	0.02				1,18
Tropical tropopause	0.7						2
Arctic tropopause, 68°N	0 - 0.84						2
Midlatitude	1.1	0.14					15
Midlatitude	0.76	0.16	0.07	0.07	0.32		16
Tropical Pacific, 4 to 6 km	0.80		0.10	0.09	0.44		16
Tropical Pacific, > 10 km	0.76		0.07	0.07	0.32		16

* Data taken from graph.

References:

¹Schauffler *et al.*, 1993; ²Kourtidis *et al.*, 1996; ³Atlas *et al.*, 1993; ⁴Atlas *et al.*, 1992; ⁵Bottenheim *et al.*, 1990; ⁶Reifenhäuser and Heumann, 1992; ⁷Yokouchi *et al.*, 1997; ⁸Yokouchi *et al.*, 1994; ⁹Yokouchi *et al.*, 1996; ¹⁰Class and Ballschmiter, 1986b; ¹¹Schall and Heumann, 1993; ¹²Cicerone *et al.*, 1988; ¹³Penkett *et al.*, 1985; ¹⁴Atlas and Ridley, 1996; ¹⁵Wamsley *et al.*, 1998; ¹⁶Schauffler *et al.*, 1998b; ¹⁷Sturges, 1993; ¹⁸Schauffler *et al.*, 1998a.

CH_2Br_2 , and the bromochloromethanes associated with source regions (e.g., Atlas *et al.*, 1993; Yokouchi *et al.*, 1996).

Few studies have sufficient temporal coverage to examine a seasonal trend in reactive organic Br. One study (Cicerone *et al.*, 1988) reported a strong seasonal cycle in bromoform at Barrow, Alaska; a smaller magnitude seasonal cycle was observed at Cape Kumakahi, a surface coastal site on the island of Hawaii. The Arctic trend for bromoform and other bromocarbons was also seen at Alert, NWT, by Yokouchi *et al.* (1996). A winter/summer concentration ratio of 3.6, 2.1, and 1.1 was observed for CHBr_3 , CHBr_2Cl , and CH_2BrCl , respectively. A one-year study at the Mauna Loa Observatory also revealed a seasonal cycle in atmospheric bromocarbon concentration (Atlas and Ridley, 1996). Interestingly, the seasonality observed at this site in the Pacific free troposphere was similar to that observed in the Arctic. Winter/summer concentration ratios of 2.8, 2.0, 1.4, and 1.3 were observed at Mauna Loa for CHBr_3 , CHBr_2Cl , CHBrCl_2 , and CH_2BrCl , respectively. The seasonality in shorter-lived organic Br at these sites represents differences resulting from source and transport variations and seasonality in loss processes (see below). No long-term temporal trends are evident from examination of the available datasets.

Airborne/Free Troposphere Measurements

Relatively few studies of the distributions of shorter-lived organic Br compounds in the free troposphere or into the stratosphere have been reported. Some ground-based measurements from island sites can be representative of the marine free troposphere. The measurements at Mauna Loa Observatory showed significantly lower mixing ratios of bromocarbons at the observatory site at 3.4 km compared to measurements near the island coastline. Similar island-based measurements at Tenerife (Class *et al.*, 1986; Class and Ballschmiter, 1988) also demonstrate a significant decline in bromocarbon concentrations above the marine inversion layer.

In the tropical and South Pacific atmosphere, highest mixing ratios of shorter-lived organic brominated compounds are observed in the marine boundary layer, with smaller concentrations aloft (Figure 2-11). A secondary maximum in the 6- to 8-km range may be due to convective redistribution of species. On average, 40% of the shorter-lived organic Br compounds measured in the boundary layer is still present at altitudes between 10 and 12 km. At the highest altitudes sampled, CH_2Br_2

is the most abundant of these compounds and, in total, organic Br compounds other than CH_3Br contribute about 15% to the total load of organic Br in the upper Pacific troposphere.

An unresolved issue concerning the impact of shorter-lived organic Br species on stratospheric ozone is related to their input into the upper troposphere and lower stratosphere, where they are converted to reactive inorganic forms of Br. Schauffler *et al.* (1993) and Kourtidis *et al.* (1996) report concentrations of CH_2Br_2 of about 0.7 ppt at the tropical tropopause. These measurements are consistent with the tropospheric dataset from the Pacific Exploratory Mission (PEM) Tropics (Schauffler *et al.*, 1998b). Tropopause concentrations of CH_2Br_2 were reported to be more variable in the Arctic region. A rapid decrease in CH_2Br_2 and CH_2BrCl above the tropopause has been reported (Wamsley *et al.*, 1998; Kourtidis *et al.*, 1996; Schauffler *et al.*, 1998b). Wamsley *et al.* (1998) related the concentrations of brominated organic compounds to CFC-11 and report an approximately 50% reduction in the concentration of CH_2Br_2 and CH_2BrCl relative to a 10% reduction in CFC-11. Thus, the conversion of short-lived organic Br compounds to reactive inorganic species is most significant in the tropopause region and the lower stratosphere.

The role of bromoform in the tropopause region is undetermined. Schauffler *et al.* (1998b) report a decrease in mixing ratios between 10 and 15 km at NH mid-latitudes of about 90% for CHBr_3 and about 40% for CH_2Br_2 . These data suggest that CHBr_3 is more rapidly depleted in the lower stratosphere compared to CH_2Br_2 , as may be expected from their respective photochemical loss rates. However, the available data are insufficient to estimate the rate and magnitude of reactive organic Br input to the lower stratosphere. Current data (see Table 2-7) indicate the presence of ≤ 2 ppt Br from shorter-lived organic Br compounds at the tropopause and hence place an upper limit on the amount of Br entering the tropical stratosphere. However, the potential variability in these compounds is high and the appropriate altitude range is undersampled with respect to the reactive organic species. Data are not available yet to assess how episodic convection of surface air rich in bromoform and other bromocarbons can impact chemistry in the tropopause region. It is generally assumed that all Br released in the troposphere is removed by wet scavenging; however, this assumption has not been tested by model calculations.

SHORT-LIVED COMPOUNDS

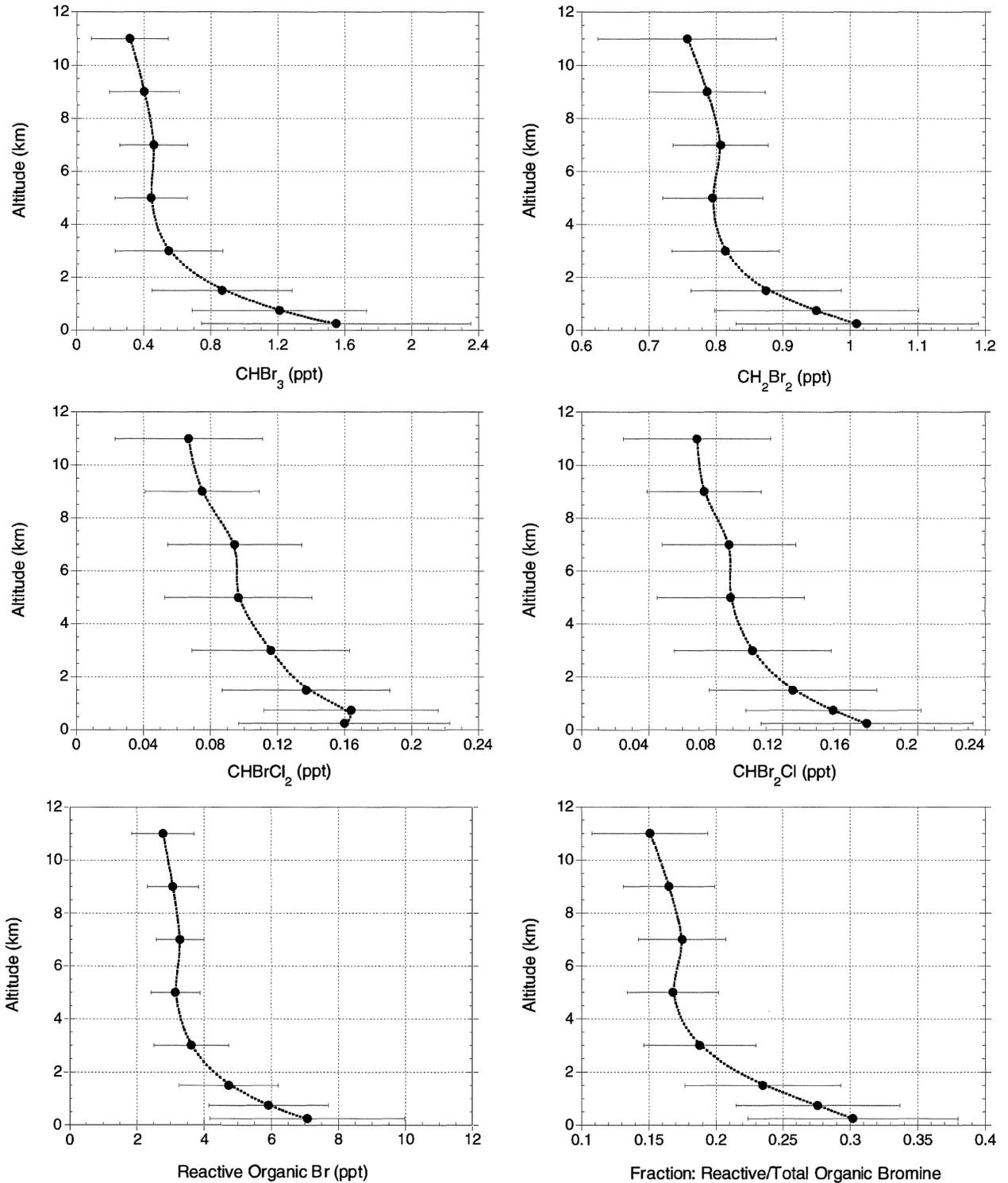


Figure 2-11. Vertical profiles of individual reactive organic Br gases, total reactive organic Br, and fraction of reactive/total organic Br over the Pacific Ocean (adapted from Schauffler *et al.*, 1998b). Mean and standard deviation are plotted.

2.3.2.2 SOURCES AND SINKS/LIFETIMES

Sources

Reactive organic Br compounds have both natural and anthropogenic sources. The anthropogenic source of bromoform and bromochloromethanes is primarily related to treatment and disinfection of drinking water and cooling waters. In addition to the trihalomethanes, several brominated acids and acetonitriles are produced in the treatment process. Gschwend *et al.* (1985) estimated a production rate of organic Br compounds from water chlorination of 0.6 Gg Br yr⁻¹ from seawater and 4 Gg yr⁻¹ from freshwater treatment. Emission of ethylene dibromide (EDB) from gasoline additives and fumigation has been significant in past decades, but there are fewer emissions today due to increased regulation of the compound. Consistent with the reduced emission, current atmospheric measurements suggest low (> 0.05 ppt) levels of EDB in the ambient atmosphere.

Natural production of reactive organic Br compounds from algal sources has been clearly demonstrated. To date, a wide range of species of macroalgae and microalgae, from temperate as well as polar regions, has been examined for organohalogen production, and analysis of algal tissues has revealed a complex suite of different organohalogen compounds (McConnell and Fenical, 1977). The relative release rates of individual organic Br compounds from different algal species can vary, and a wide variety of halocarbons can be formed, but most often bromoform is the major compound measured. There have been suggestions, too, that bromochloromethanes can be formed from chloride ion substitution of bromoform in seawater (Class and Ballschmiter, 1988), but laboratory studies indicate a clear primary source of bromochloromethanes from algae. The mechanism of bromoform production in algae has been linked to a pathway involving bromoperoxidase enzyme (Moore *et al.*, 1996a).

The magnitude of the natural organic Br source is difficult to assess. Studies of halocarbon production in laboratory systems have shown that production is species specific and apparently is quite variable within samples of the same species. Also, procedures for reporting and estimating production rates vary between different investigators. Finally, some estimate must be made of the fraction of organic Br compounds produced by algae which undergoes air-sea exchange. Sturges *et al.* (1992)

estimate that the combined annual production of organic Br from Antarctic and Arctic ice algae is in the range of 10 to 150 Gg Br. This can be contrasted to estimates of 0.08 to 36 Gg Br yr⁻¹ from macroalgae (Gschwend *et al.*, 1985; Schall *et al.*, 1994). These estimates do not include the potentially large open-ocean source associated with algal production associated with equatorial upwelling. The industrial source of bromoform and bromochloromethanes is considerably less than these estimates (4.6 Gg). Overall, algal production of reactive organic Br compounds is the same order of magnitude as that estimated for halon and CH₃Br emission (see Chapter 1 and Section 2.3).

Sinks/Lifetimes

The reactive organic Br compounds discussed here have photochemical sinks from photolysis and OH and Cl oxidation. Rate constants for the OH reactions, which constitute the most important tropospheric oxidative loss processes, are summarized in Table 2-8. Using these rate constants and measured photolysis cross sections, an approximate photochemical lifetime has been estimated (Table 2-9). These calculations indicate that photolytic loss is most important for bromoform, oxidation by OH controls the lifetimes of CH₂BrCl and CH₂Br₂, and both OH oxidation and photolysis are significant for CHBrCl₂ and CHBr₂Cl. The lifetimes calculated here can be used to provide another estimate of the surface flux of reactive organic Br compounds. Assuming a total atmospheric loss rate based on OH reaction and photolysis (Table 2-9) and a global average concentration for CHBr₃ and CH₂Br₂ of 0.4 and 0.8 ppt, respectively, and 0.1 ppt for CH₂BrCl, CHBrCl₂, and CHBr₂Cl (see Table 2-7), we approximate fluxes of slightly greater than 270 Gg yr⁻¹ of Br from these reactive organic species. We note that this calculation necessarily provides only a rough estimate of the Br flux because of the uncertainty in the spatial and seasonal distributions of reactive organic Br compounds. A more comprehensive model is required to more accurately assess the global flux of reactive organic Br compounds. Still, the estimated fluxes may not be inconsistent with emission estimates from algal production reported above, and reinforce the idea that approximately 50 to 65% of the flux of all organic Br is related to natural emission of short-lived bromocarbon gases. This provides another upper bound for the flux of Br delivered to the stratosphere.

SHORT-LIVED COMPOUNDS

Table 2-8. Rate constants for OH reactions with short-lived organic Br compounds.

Compound	OH Rate Constant ($\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$)		
	$k(T)$	$k(298)$	Ref.
CH_2BrCl	$2.3 \times 10^{-12} \exp(-930/T)$	1.0×10^{-13}	1
CH_2Br_2	$2.4 \times 10^{-12} \exp(-900/T)$	1.2×10^{-13}	1
CHBrCl_2	-	1.2×10^{-13}	2
CHBr_2Cl	-	1.2×10^{-13}	est'd
CHBr_3	$1.6 \times 10^{-12} \exp(-710/T)$	1.5×10^{-13}	1

¹ DeMore *et al.*, 1997.

² Bilde *et al.*, 1998.

Table 2-9. Approximate tropospheric lifetimes and fluxes.

Compound	Lifetime		[X] (ppt Br) [†]	Flux (Gg Br yr ⁻¹)
	OH Reaction*	Photolysis**		
CH_2BrCl	150 days	15000 days	0.1	2.9
CH_2Br_2	130 days	5000 days	1.6	53.7
CHBrCl_2	(120) days ^{††}	222 days	0.1	5.5
CHBr_2Cl	(120) days ^{††}	161 days	0.2	12.4
CHBr_3	100 days	36 days	1.2	196.5

* Lifetimes calculated for $T = 275 \text{ K}$, $[\text{OH}] = 1 \times 10^6 \text{ molecule cm}^{-3}$.

** Photolysis lifetimes based on globally and seasonally averaged J-value estimated for 5 km.

† Estimated global average mixing ratio as ppt-Br.

†† T-dependence of OH rate is estimated.

2.4 IODINATED COMPOUNDS

For iodine, the efficiency for ozone removal is much larger per molecule than that of Cl or even Br. This is due to the fact that essentially all of inorganic iodine is expected to be in the active form IO_x , and the rate-limiting reactions for catalytic removal (i.e., reactions of IO with HO_2 , ClO, and BrO) are faster than the corresponding Cl and Br reactions. Iodine chemistry has recently been invoked to help understand lower stratospheric and upper tropospheric ozone levels. Modeling results reported by Solomon *et al.* (1994) suggested that IO reactions could be playing an important causal role in the decadal trends in ozone currently observed (see Section 7.6.2). Davis *et al.* (1996) report model results that indicate that under certain conditions, iodine chemistry could significantly impact the rate of destruction of upper tropospheric ozone.

2.4.1 Methyl Iodide (CH_3I)

The main source of methyl iodide (CH_3I) is thought to be oceanic (Chameides and Davis, 1980), with some impact from biomass burning (Andreae *et al.*, 1996; N.J. Blake *et al.*, 1996). Work by Happell and Wallace (1996) and Moore and Zafiriou (1994) suggests that photochemical processes dominate marine CH_3I production and that the ocean is most likely a sink at high latitudes and during winter, and a source only at low latitudes and during summer. Blake *et al.* (1997) discuss latitudinal and vertical profiles obtained during two Pacific-region airborne missions flown in the summer of 1991 and winter of 1994. They report that, during summer, marine boundary layer mixing ratios in the 0.5- to 1.0-ppt range were observed in the northern Pacific, whereas in the winter this range was encountered only in or near the tropics. Marine hot spots exceeding

1 ppt occurred during both seasons. During the 1992 Polar Sunrise Experiment, Yokouchi *et al.* (1996) observed wintertime CH_3I values of 1 to 1.5 ppt, whereas the springtime concentrations were in the 0.6- to 0.3-ppt range. Blake *et al.* (1998) report seasonal changes in CH_3I concentrations near Tasmania. The CH_3I levels increased as summer approached, the opposite of what Yokouchi *et al.* (1996) observed. Davis *et al.* (1996) report CH_3I concentrations obtained during a summer 1991 airborne mission; a significant amount of their Asian Pacific study area was under the influence of rapid vertical transport resulting from numerous typhoons. They report CH_3I mixing ratios in excess of 1 ppt at altitudes of 12 km. They also indicate that some typhoons had cloud tops at altitudes greater than 18 km and likely transported significant amounts of marine boundary layer air into the lower stratosphere. Although CH_3I mixing ratios in coastal waters can be quite elevated (Oram and Penkett (1994) reported 43 ppt), generally over the open ocean the concentrations range between 0.1 and 2 ppt (Atlas *et al.*, 1993; Yokouchi *et al.*, 1996, 1997; D.R. Blake *et al.*, 1996; Blake *et al.*, 1997, 1998).

Wennberg *et al.* (1997) studied the IO absorption observed in high-resolution, high-airmass solar spectra taken at the Kitt Peak National Solar Observatory, Arizona. Their results suggest that the total stratospheric iodine mixing ratio is 0.2 (+0.3, -0.2) ppt, thus limiting its contribution to ozone depletion in the lower stratosphere. This is consistent with reported upper tropospheric CH_3I mixing ratios of 0.05 to 0.2 ppt (Blake *et al.*, 1997) and with upper limits of 0.1 to 0.2 ppt in the 15- to 20-km region (Pundt *et al.*, 1997). The only significant removal process for CH_3I is photolysis. Roehl *et al.* (1997) report the ultraviolet absorption spectra of a number of alkyl halides. They calculate that the surface photolysis rate constant at a solar zenith angle of 40° for CH_3I is approximately 4 days and decreases to about 1.5 days at 10 km. No CH_3I trend studies have been published.

2.4.2 Ethyl Iodide ($\text{C}_2\text{H}_5\text{I}$) and Other Iodocarbons

Atmospheric data are scarce for iodocarbons other than CH_3I . During a western Pacific cruise, Yokouchi *et al.* (1997) observed ethyl iodide ($\text{C}_2\text{H}_5\text{I}$) at mixing ratios of 0 to 0.3 ppt. During the same time CH_3I was in the 0.4- to 2-ppt range. The photolysis rate for ethyl iodide is slightly faster than that of CH_3I (Roehl *et al.*, 1997). Thus, ethyl iodide has a slightly shorter photolytic

lifetime than CH_3I (Table 2-4). Additional surface and airborne studies are needed in order to determine if ethyl iodide emissions at some locations are large enough for it to play a role in upper tropospheric/lower stratospheric ozone chemistry.

A number of shorter-lived iodocarbons have been observed. Chloriodomethane (CH_2ClI) has a typical photolytic lifetime of about two hours (Table 2-4). Yokouchi *et al.* (1996) observed an annual cycle in chloriodomethane in the Arctic, with peak levels of 0.05 ppt during winter and undetectable levels (< 0.005 ppt) in summer. Schall and Heumann (1993) reported 0.07 ppt (ranging from less than 0.004 to 0.18 ppt) of chloriodomethane during September in Spitzbergen. Undetectable levels were reported by Yokouchi *et al.* (1997) during the western Pacific cruise mentioned above. Other reported iodocarbons include diiodomethane (CH_2I_2), isopropyl iodide ($\text{CH}_3\text{CHICH}_3$), and n-propyl iodide ($\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$), with concentrations ranging from tenths to several ppt (Schall and Heumann, 1993). All have photolytic lifetimes less than ethyl iodide, with diiodomethane having a lifetime on the order of minutes (Table 2-4). All of the above organoiodine compounds are believed to be of natural origin. One human-made iodocarbon, CF_3I , has been developed as a potential halon replacement (Solomon *et al.*, 1994). It has a lifetime of about 1 day (Table 2-4). There are no known reports of its occurrence in the atmosphere.

2.5 OTHER OZONE-RELATED COMPOUNDS

In this section we discuss the atmospheric budgets of methane (CH_4) and carbon monoxide (CO). CH_4 plays an important role both as a greenhouse gas and a reactive tropospheric and stratospheric chemical species. In the troposphere, CH_4 is a source of OH radicals produced via its reaction with excited oxygen atoms, $\text{O}(^1\text{D})$, and also is an OH sink. In the stratosphere, CH_4 controls the abundance of Cl atoms by converting them to HCl. CO also plays an important chemical role in the troposphere by converting OH radicals into HO_2 .

2.5.1 Methane (CH_4)

2.5.1.1 RECENT TRENDS

The burden of atmospheric CH_4 continues to increase, but the rate of growth of this burden is declining (Dlugokencky *et al.*, 1994a; Matsueda *et al.*, 1996). Recent measurements indicate growth rates of about 3

SHORT-LIVED COMPOUNDS

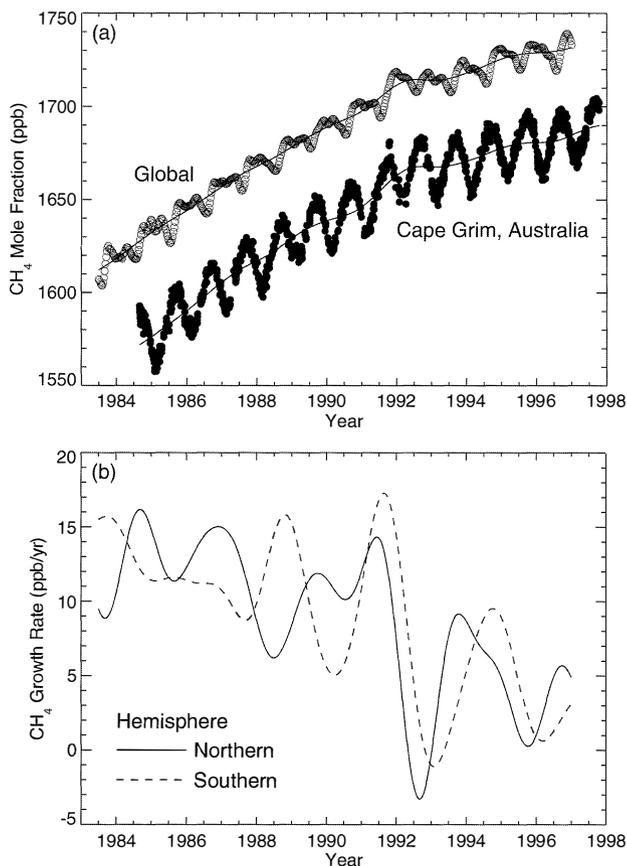


Figure 2-12. (a) Globally averaged CH₄ mole fractions (open symbols). The averages are determined by smoothing the measurements from the NOAA/CMDL cooperative air sampling network in time and latitude (see Dlugokencky *et al.*, 1994a, 1998, for details). Also shown are atmospheric CH₄ mole fractions determined from discrete samples collected at Cape Grim, Tasmania, after selection for baseline conditions (closed symbols) (Steele *et al.*, 1996). In both cases, the solid line represents the long-term trend. (b) Instantaneous growth rate curves determined from zonal averages for NH (solid line) and SH (dashed line) (Dlugokencky *et al.*, 1994a, 1998).

to 4 ppb yr⁻¹ in the 1996 to 1997 period (Dlugokencky *et al.*, 1998; Steele *et al.*, 1996) (see Figures 2-12 and 2-13). Apart from the anomalously low growth rates during 1992/93 (Dlugokencky *et al.*, 1994b, 1996), the growth rate of CH₄ is now at its lowest value since the 1940s (Figure 2-14), as indicated by the recent analysis by Etheridge *et al.* (1998). In their analysis, CH₄ data from

three Antarctic ice cores, Antarctic firm air, the Cape Grim (Tasmania) Air Archive (CGAA) dating back to 1978 (Langenfelds *et al.*, 1996a), and direct atmospheric measurements since 1984 have been combined to present a very high time resolution record of atmospheric CH₄ from 1000 AD to the present. An analysis of the NOAA/CMDL global CH₄ dataset by Dlugokencky *et al.* (1998) suggests that the observed decrease in the growth rate of CH₄ over the period of their data (1984 to 1996) is consistent with an approach to steady state, where both the total global source of CH₄ and the average OH concentration have stayed nearly constant over this period. They conclude that “Unless the global CH₄ budget changes, the globally averaged CH₄ mole fraction will slowly increase to about 1800 ppb, and the contribution of CH₄ to the greenhouse effect will not increase significantly above its current level.” It would seem to be appropriate that the large body of observational evidence now showing declining growth rates of CH₄ since the early 1980s be reflected in the range of emission scenarios being used in model simulations of climate over the next century.

Further analysis of the period of low CH₄ growth in 1992/93 has been reported by Dlugokencky *et al.* (1996). They show that following the eruption of Mt. Pinatubo in June 1991, there were sudden temporary increases in the growth rates of both CH₄ and CO in the tropics and high southern latitudes. Calculations made with a radiative-transfer model showed that ultraviolet (UV) actinic flux in the 290- to 330-nm wavelength region was attenuated by about 12% immediately after the eruption due to absorption by SO₂ and scattering by sulfate aerosols. Dlugokencky *et al.* (1996) suggest that decreased UV penetration into the troposphere led to a decrease in OH and subsequent increases in the growth rates of both CH₄ and CO. The enhanced growth rates during late 1991 and early 1992 were then followed by very low growth rates in 1992/93. It has been suggested that these low growth rates were due to the cooler temperatures following the Mt. Pinatubo eruption causing lower CH₄ emissions from NH wetlands (Hogan and Harriss, 1994). It also has been suggested that volcanic aerosols injected into the lower tropical stratosphere from Mt. Pinatubo induced changes in stratospheric circulation that impacted tropospheric CH₄ trends (Schauffler and Daniel, 1994). The features described above also have been observed in vertical column abundance measurements of CH₄ at the Jungfraujoch station between the mid-1980s and April 1997. That database indicates mean

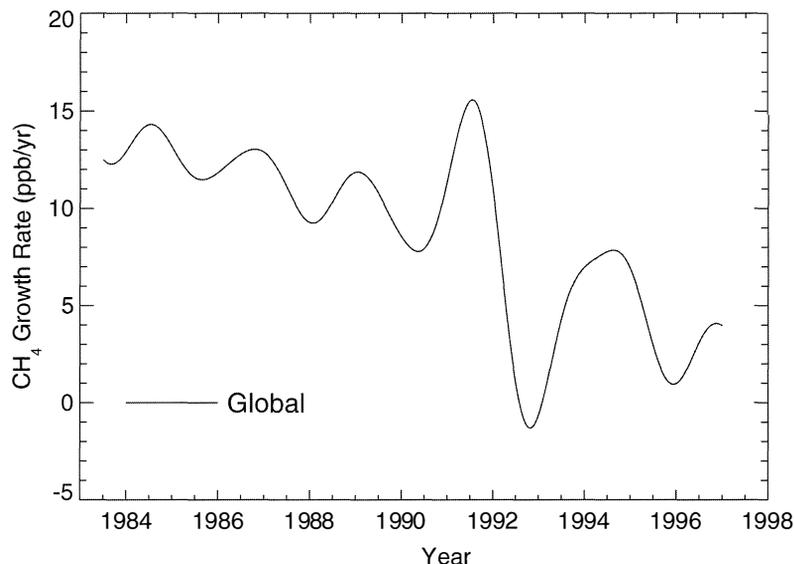


Figure 2-13. Growth rate calculated as the derivative of the long-term trend line shown for the NOAA/CMDL global CH_4 averages in Figure 2-12.

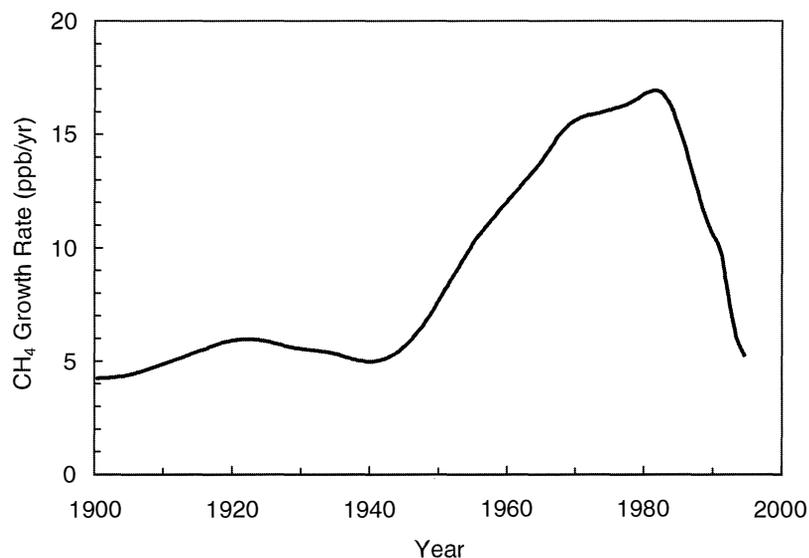


Figure 2-14. Global CH_4 growth rate for the period 1900 to 1995 from Etheridge *et al.* (1998). It was calculated as the derivative of a curve fitted to CH_4 measurements from Antarctic ice cores, Antarctic firn air, and Cape Grim air, after an adjustment of the measurements to global values.

rates of increase prior to and after January 1991 equal to $0.73\% \text{ yr}^{-1}$ and $0.44\% \text{ yr}^{-1}$, respectively (Zander *et al.*, 1997).

Paleo records of atmospheric CH_4 have been recently updated and improved. A high-resolution record over the Holocene (the last 11,500 years) derived from both Antarctic and Greenland ice cores has been presented by Chappellaz *et al.* (1997). They find an average inter-polar difference of 44 ± 7 ppb, compared with a present-day inter-polar difference of 143 ± 1 ppb derived from the NOAA/CMDL global data (Dlugokencky *et al.*, 1994a). The variations in the

inter-polar difference over the Holocene are interpreted with a three-box model of the atmosphere to indicate variations with time in the magnitudes of tropical and high-northern-latitude sources of CH_4 . Using very high time resolution ice cores from Antarctica, Etheridge *et al.* (1998) have determined the global average CH_4 mixing ratio during the late preindustrial Holocene (1000 to 1800 AD) to be 695 ppb, with variations around this value of up to 40 ppb. These variations are strongly correlated with indicators of climate variation and serve to emphasize that it is inappropriate to represent the preindustrial level of atmospheric CH_4 by a single value.

SHORT-LIVED COMPOUNDS

Table 2-10. Global budget of CH₄.

Source or Sink	Magnitude (Tg yr ⁻¹)		
	WMO (1995)	Fung <i>et al.</i> (1991) ^a	Hein <i>et al.</i> (1997) ^b
<u>Sources</u>			
Wetlands	110	115	237
Termites	20	20	-
Ocean	10	10	-
Freshwater	5		-
Hydrates	10	5	-
Energy-related	100	75	97
Sewage treatment	25	-	-
Landfills	30	40	35
Animal waste	25	80	90
Ruminants	80		
Biomass burning	40	55	40
Rice paddies	60	100	88
Total Sources	515	500	587
<u>Sinks</u>			
Soils	30	10	-
Reaction with OH	445	450	489
Removal in stratosphere	40		46
Total Sinks	515	460	535

^a Scenario preferred by Fung *et al.* (1991) as a fit to a 1984 to 1987 database.

^b Fit to a 1991 to 1993 database.

A notable development over recent years has been the increase in the number and range of aircraft-based observations of CH₄. Vertical profiles of CH₄ from the surface to an altitude of about 8 km near Cape Grim, Tasmania (41°S), have been measured approximately monthly since 1991 (Langenfels *et al.*, 1996b). These data sometimes show strong average vertical gradients (about 20 ppb higher at 8 km than at the surface), particularly during the austral summer (Pak *et al.*, 1996), and possibly are signatures of biomass burning plumes from Africa and South America. Similar vertical gradients were observed by Bartlett *et al.* (1996) during research flights over the south Atlantic Ocean during September to October 1992.

Airborne measurements of CH₄ over western Siberia in August 1994 showed highly elevated levels near oil production sites or pipelines, suggesting leakage of natural gas (Tohjima *et al.*, 1996). Regular measurements of

atmospheric CH₄ are being made from a Boeing 747 commercial airliner flying between Japan and Australia (Matsueda and Inoue, 1996). Another important method for obtaining information on trace gas budgets, including that of CH₄, has been recently described (Crutzen *et al.*, 1998). By making measurements from a laboratory wagon traveling along the Trans-Siberian railroad, these investigators have demonstrated an elegant way of collecting such data from the vast continental area of Russia, a region for which there has been relatively little data in the past, and which is needed to supplement the largely marine boundary layer datasets available to now.

2.5.1.2 SOURCES AND SINKS

Current knowledge on the sources and sinks of CH₄ has been summarized and discussed in previous assessments (WMO, 1995; IPCC, 1995). Recently revised budgets of atmospheric CH₄ are broadly similar to those

published previously (Hein *et al.*, 1997). Most individual CH₄ source terms continue to have relatively large uncertainties. Using an inverse modeling approach, Hein *et al.* (1997) found that the average uncertainty of the magnitudes of CH₄ sources could be reduced by at least one-third using the present observational network. Table 2-10 shows the “best” estimates for the magnitude of the different sources and sinks for CH₄, as given in WMO (1995), compared to the values derived and preferred by Fung *et al.* (1991) and Hein *et al.* (1997) using inverse modeling methods. Differences in estimates reflect the sensitivity of inverse methods to the assumed geographical distribution of sources and sinks, and the inclusion of specific minor processes. Further reductions in the uncertainties almost certainly will require additional observations near source regions.

Improvements in the knowledge of the CH₄ budget have come from a more accurate estimation of the lifetime of CH₄ due to removal by OH (Prinn *et al.*, 1995). The new total atmospheric lifetime value of 8.9 ± 0.6 years is lower than the previous estimate of 10.0 years and is based upon a new calibration scale for CH₃CCl₃ measurements and a good knowledge of the respective reaction rate constants with OH. The adjustment time for CH₄ recovery would be somewhat longer due to CH₄ feedback on CO and OH (see Chapter 2 in WMO, 1995).

The question of whether Cl atoms significantly influence the oxidizing capacity of the atmosphere is addressed by studies of tetrachloroethylene (C₂Cl₄). This chemical is known to react about 300 times faster with Cl atoms than with OH. Analyses of C₂Cl₄ measurement data in the context of a global 2-D atmospheric model indicate that Cl atoms are likely to enhance CH₄ oxidation by less than 2% (Singh *et al.*, 1996; Rudolph *et al.*, 1996).

2.5.2 Carbon Monoxide (CO)

2.5.2.1 ATMOSPHERIC DISTRIBUTIONS

Surface Measurements

Over the past several years the number of CO monitoring sites in both the background and regionally polluted troposphere have continued to increase. The NOAA/CMDL cooperative air sampling network established new sites chosen to study regions impacted by pollution in the United States, Europe, Africa, and Asia. These non-background sites typically show greater winter mixing ratios than background sites at similar latitude, whereas levels in summertime are often similar

(Novelli *et al.*, 1998a). In the background atmosphere, measurements of CO in air collected at several sites on Antarctica now extend the global network from 82°N to 90°S. Background CO mixing ratios range from a high of 200 to 225 ppb in winter in the high northern latitudes to a low of 40 to 50 ppb during summer in the high southern latitudes. The WMO has proceeded with the Global Atmospheric Watch (GAW) program, which has established Global Environmental Facilities (GEF) to provide continuous or semi-continuous monitoring of CO at six locations (China, Indonesia, Brazil, Argentina, Algeria, Kenya) (WMO, 1995). Measurements of CO are currently made at the GAW/GEF sites in Argentina and China; grab samples from these sites are collected for analysis at CMDL to provide comparison of the datasets. Samples of air are also collected by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) at the WMO site in Indonesia for trace-gas analysis.

In the background atmosphere, spatial distributions of CO in the marine boundary layer (MBL) have become better defined. CO is well mixed in the high latitudes of both hemispheres, with times series from widely separated sites nearly indistinguishable. Time series from the tropics and extratropics show both greater short-term and interannual variations, which is attributed to their proximity to surface sources. CO mixing ratios in the MBL continue to decline, with values in the high SH now often reaching seasonal minimums below 40 ppb (Novelli *et al.*, 1998a). Issues of calibration and the consistency of measurements between laboratories remain a concern. Data from different laboratories should not be combined until measurements are compared. A recent intercomparison of standards as part of the Measurement of Air Pollution from Satellite (MAPS) validation revealed that differences up to 50% may still exist between laboratories (Novelli *et al.*, 1998b).

Middle and Upper Troposphere

Compared to the boundary layer, less is known about the distributions and seasonal cycles of CO in the middle and upper troposphere. Long-term measurements of the vertical profiles of trace gases above Carr, Colorado (Bakwin *et al.*, 1994), and Cape Grim, Tasmania (Pak *et al.*, 1996), have helped define differences in CO between the surface and middle troposphere in the two hemispheres. At Carr, CO tends to decrease with altitude, often with clearly defined layers of higher CO and other carbon gases such as carbon

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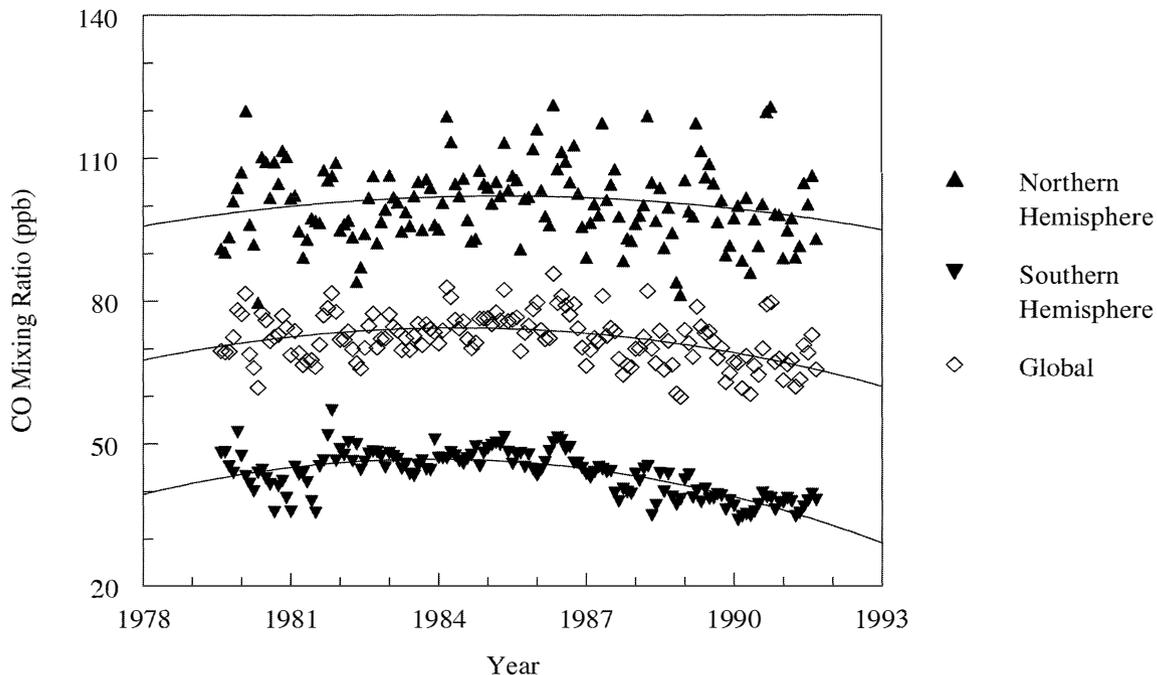


Figure 2-15. Zonally averaged, deseasonalized CO mixing ratios (from six sites 70°N to 90°S). Estimated average trends (ppb yr⁻¹) between 1981 and 1986: global = 0.9 ± 0.4 , NH = 0.8 ± 0.7 , SH = $1.0 \pm .4$; between 1986 and 1992: global = -1.8 ± 0.5 , NH = -1.3 ± 0.9 , SH = -2.3 ± 0.3 . Reprinted with permission from *Nature*. (Khalil, M. A. K., and R. A. Rasmussen, Figure 1b, Trends from Table 1, *Nature*, 370, pp. 639-640, copyright 1994, MacMillan Magazines Limited.)

dioxide (CO₂) and CH₄. At Cape Grim, CO typically increases with altitude all year long, with a strong seasonal maximum in spring. Such measurements show that significant amounts of CO, produced at the surface by biomass burning, are transported above the boundary layer into the middle troposphere. Thus, the networks that measure CO in the planetary boundary layer see only a part of the annual cycle of this gas. Additional locations of vertical profiles are planned under the Measurement Of Pollution In The Troposphere (MOPITT) validation. Regular measurements from a commercial jet between Japan and Australia show strong seasonal cycles in both hemispheres, with surprisingly strong CO enhancement in the southern extratropics between 9 and 12 km during the spring (Matseuda *et al.*, 1998).

Measurements of CO from space have advanced. The MAPS Space Shuttle instrument has a maximum CO signal at approximately 300 mb. MAPS was flown for 10-day missions during April and October, 1994,

during which time nearly global distributions were determined. Modifications to the instrument and data retrieval procedures indicated that the large bias error in the earlier flights was reduced to about 10% (Reichle *et al.*, 1990, 1998). MAPS showed very high levels of CO over the tropical south Atlantic, southern Africa and Indochina, which likely reflected transport of emissions from surface fires into the middle troposphere (Newell *et al.*, 1998). Scheduled for launch as part of the EOS/MTPE AM-1 (Earth Observing System - Mission to Planet Earth *ante meridian* equatorial crossing) satellite, MOPITT promises to define global tropospheric CO averaged mixing ratios at three to four altitude ranges, extending from the surface to 15 km (Drummond, 1992). An extensive validation program will include in situ measurements of CO vertical profiles from aircraft and vertical column abundances from ground-based solar observations.

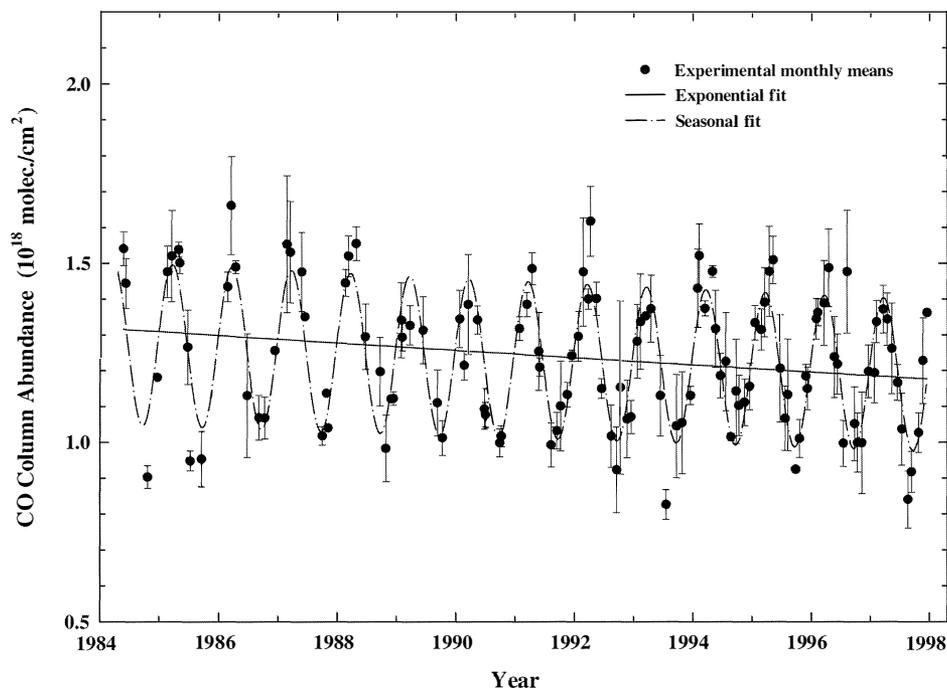


Figure 2-16. Vertical column abundances of CO monitored above the Jungfraujoch. The monthly means shown are adapted from the daily data given in Mahieu *et al.* (1997), with the data extended through the end of 1997. Both the seasonal and exponential fits to the data are shown. The trend derived from an [exponential + sine] fit is $-0.53 \pm 0.18\% \text{ yr}^{-1}$, whereas an exponential fit alone (shown by the solid line) yields $-0.82 \pm 0.34\% \text{ yr}^{-1}$.

2.5.2.2 TRENDS

CO mixing ratios at sites around the world show considerable interannual variation. Whereas this may be attributed in part to variations in transport (Allen *et al.*, 1996), the average global changes represent changes in sources and sinks. Although the evaluation of long-term trends in CO are limited by the available measurements, comparisons of solar spectra determined during 1950 to 1951 above Switzerland to measurements made in the mid-1980s at the same site suggested a linear rate of increase of column CO of slightly less than $1\% \text{ yr}^{-1}$ (Zander *et al.*, 1989). Time series determined at six sites, three in the NH and three in the SH, indicated a similar rate of increase in the early to mid-1980s (Khalil and Rasmussen, 1988). CO measurements in Greenland ice cores suggest that there has been an increase in the high NH since 1850, whereas samples from Antarctica show no trend (Haan *et al.*, 1996). Monitoring of CO at Cape Point, South Africa, since 1979 have shown periods

of CO increase and decrease, with no significant trend discernible.

This trend of increasing CO appears to have reversed in the late 1980s (Figure 2-15). Since then, CO is reported to have decreased at surface sites in both hemispheres (Khalil and Rasmussen, 1994; Novelli *et al.*, 1994). A decrease in CO is also evident in the atmospheric column above Europe (Figure 2-16) (Zander *et al.*, 1994b; Mahieu *et al.*, 1997). The NOAA/CMDL record shows a sharp global decrease during late 1991 through mid-1993 (Novelli *et al.*, 1998a). After a short period of increased growth rate in the second half of 1991 (see Section 2.5.1.1 for analogous discussion of CH_4), CO decreased rapidly. This decline has been attributed, in part, to an increase in tropospheric OH resulting from a decrease in stratospheric ozone following the Mt. Pinatubo eruption (Granier *et al.*, 1996). Particularly low levels of biomass burning in 1992 may also have contributed to the CO decrease. Comparison of recent time series determined in the SH by different laboratories

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Table 2-11. Global budget of CO. (Adapted from IPCC (1995) except where noted.)

Sources	Magnitude (Tg yr ⁻¹)	Sinks	Magnitude (Tg yr ⁻¹)
Fossil fuels and industry	300 to 500	Reaction w/ OH ^a	1400 to 3000
Biomass burning	300 to 700	Removal in the stratosphere	~100
CH ₄ oxidation	400 to 800	Soil uptake ^b	100 to 600
NMHC oxidation	200 to 600		
Oceans	20 to 200		
Vegetation ^c	20 to 200		
Total Sources	1240 to 3000	Total Sinks	1600 to 3700

^a Reflects increased estimates of the atmospheric concentration of OH (Prinn *et al.*, 1995).

^b Lower end of range includes recent results of Sanhueza *et al.* (1998) and Potter *et al.* (1996).

^c Badr and Probert, 1994.

shows significant differences. Time series from Cape Grim, Tasmania, determined by NOAA/CMDL and CSIRO show similar features, but of different magnitudes. Both records show declines in CO from late 1991 to mid-1993, though the NOAA/CMDL time series shows a sharper decrease. This change is not evident in the Cape Point record (Scheel *et al.*, 1996). At Cape Grim, partial (NOAA/CMDL) to full (CSIRO) recovery in CO occurred during 1993 to 1995 (Novelli *et al.*, 1998a; Steele *et al.*, 1996).

The consistency and breadth of CO measurements have improved in recent years. However, given the considerable interannual variability in CO as well as unresolved differences in measurements, predictions of future long-term trends remain uncertain.

2.5.2.3 THE GLOBAL BUDGET

There continue to be considerable uncertainties in the CO budget. Although fossil fuel combustion, biomass burning, and the oxidation of CH₄ are considered the major sources, the range of emissions still remains large (Table 2-11). The source of CO from the oxidation of nonmethane hydrocarbons (NMHC) has been reduced based upon evidence that on average, one, rather than three, CO are produced from the oxidation of isoprene (Jacob and Wofsy, 1990). No new studies have narrowed the uncertainty on the CO + OH reaction rate constant ($\pm 30\%$) which, combined with the error associated with global concentrations of OH derived from CH₃CCl₃ analysis, provide a range of estimates of the global sink

between 1400 to 2600 Tg yr⁻¹. Additional uncertainty in the sink comes from the magnitude of soil uptake.

The most significant sources and sinks of CO have been identified; however, the budget is limited by a lack of emission data and the unavailability of atmospheric distributions for many areas. More measurements and statistical emission data are needed to constrain the CO budget. Trends in emissions can be used in chemical models to examine the effects on atmospheric composition. The measured isotopic partitioning of carbon in CO (Manning *et al.*, 1997) provides additional constraints that could reduce budget uncertainties. However, at present the limited geographical extent of the isotopic data makes global extrapolations using such an analysis difficult.

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