

# CHAPTER 10

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## Methyl Bromide

**Lead Author:**

S.A. Penkett

**Co-authors:**

J.H. Butler

M.J. Kurylo

C.E. Reeves

J.M. Rodriguez

H. Singh

D. Toohey

R. Weiss

**Contributors:**

M.O. Andreae

N.J. Blake

R.J. Cicerone

T. Duafala

A. Golombek

M.A.K. Khalil

J.S. Levine

M.J. Molina

S.M. Schauffler

# CHAPTER 10

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## SCIENTIFIC SUMMARY

- Four potentially major sources for atmospheric methyl bromide ( $\text{CH}_3\text{Br}$ ) have been identified: the ocean, which is a natural source, and three others that are almost entirely anthropogenic; these are agricultural usage, which has been reaffirmed, biomass burning, which is newly recognized, and the exhaust of automobiles using leaded gasoline.
- The estimated uncertainty range for these sources is large, with oceans ranging from 60 to 160 ktonnes/yr, agriculture from 20 to 60 ktonnes/yr, biomass burning from 10 to 50 ktonnes/yr, and automobile exhaust from 0.5 to 22 ktonnes/yr. In the latter case, the range results from two conflicting assessments, which yield 0.5 to 1.5 ktonnes/yr and 9 to 22 ktonnes/yr, respectively.
- There are also two minor anthropogenic sources, structural fumigation (4 ktonnes/yr) and industrial emissions (2 ktonnes/yr), each of which are well quantified.
- Measurements of  $\text{CH}_3\text{Br}$  yield a global average ground-level atmospheric mixing ratio of approximately 11 pptv. These measurements also have confirmed that the concentration in the Northern Hemisphere is higher by about 30% than the concentration in the Southern Hemisphere (interhemispheric ratio of 1.3). Such a ratio requires that the value of sources minus sinks in the Northern Hemisphere exceeds the same term in the Southern Hemisphere.
- There is no clear long-term change in the concentration of  $\text{CH}_3\text{Br}$  during the time period of the systematic continued measurements (1978-1992). One possible explanation is that  $\text{CH}_3\text{Br}$  from automobiles may have declined while, at the same time, emissions from agricultural use may have increased, leading to relatively constant anthropogenic emissions over the last decade.
- The magnitude of the atmospheric sink of  $\text{CH}_3\text{Br}$  due to gas phase chemistry is well known and leads to a lifetime of  $2 \pm 0.5$  yr. The recently postulated oceanic sink leads to a calculated atmospheric lifetime due to oceanic hydrolysis of 3.7 yr, but there are large uncertainties (1.3 to 14 yr). Thus the overall atmospheric lifetime due to both of these processes is 1.3 yr with a range of 0.8 to 1.7 yr.
- Recognizing the quoted uncertainties in the size of the individual sources of  $\text{CH}_3\text{Br}$ , the most likely estimate is that about 40% of the source is anthropogenic. The major uncertainty in this number is the size of the ocean source. Based on the present atmospheric mixing ratio and the current source estimate, a lifetime of less than 0.6 yr would require identification of new major sources and sinks.
- The chemistry of ozone destruction by bromine in the stratosphere is now better understood. A high rate coefficient for the  $\text{HO}_2 + \text{BrO}$  reaction is confirmed and there is no evidence that it produces HBr. A conservative upper limit of 2% can be placed on the reaction channel yielding HBr. Stratospheric measurements confirm that the concentration of HBr is very low (less than 1 pptv) and that it is not a significant bromine reservoir.
- The combined efficiency of the bromine removal cycles for ozone ( $\text{HO}_2 + \text{BrO}$  and  $\text{ClO} + \text{BrO}$ ) is likely to be about 50 times greater than the efficiency of known chlorine removal cycles on an atom-for-atom basis.
- The calculated Ozone Depletion Potential (ODP) for  $\text{CH}_3\text{Br}$  is currently estimated to be 0.6 based on an atmospheric lifetime of 1.3 years. The range of uncertainties in the parameters associated with the ODP calculation places a lower limit on the ODP of 0.3.

## 10.1 INTRODUCTION

Bromine atoms are highly effective in removing ozone in the stratosphere through catalytic cycles involving free radicals such as BrO and ClO. In fact the bromine atoms remove ozone more effectively than chlorine atoms on an atom-for-atom basis, because the large majority of the inorganic bromine is in a more labile form capable of taking part in the ozone removal cycles. This is discussed in more detail in Section 10.7.

The role of bromine in the distribution of stratospheric ozone has assumed greater prominence in the past few years due to the re-evaluation upwards in the efficiency of the reaction  $\text{HO}_2 + \text{BrO}$ , which cycles BrO radicals back to bromine atoms, and due to the probability that a sizeable fraction of the main bromine source gas to the stratosphere, methyl bromide ( $\text{CH}_3\text{Br}$ ), is of anthropogenic origin. Overall, the impact on ozone of approximately 20 pptv of inorganic bromine in the stratosphere could be equivalent to about 1000 pptv of inorganic chlorine. This compares with a present total of inorganic chlorine in the stratosphere in the range of 3500 pptv.

Bromine is carried into the stratosphere in various forms such as halons and substituted hydrocarbons, of which  $\text{CH}_3\text{Br}$  is the predominant form. The halons are rather stable in the troposphere, and their production for consumption in developed countries ceased on 31 December 1993, under the latest Amendments to the Montreal Protocol. Methyl bromide, on the other hand, is much less stable in the troposphere and limitations to its emission could have a rapid impact on the amount of bromine carried into the stratosphere in this form. At present,  $\text{CH}_3\text{Br}$  production for consumption in developed countries is capped at 1991 levels beginning in 1995 under the terms of the Montreal Protocol. The U.S. Environmental Protection Agency has recently announced a phase-out by 2001 in the U.S. based upon an Ozone Depletion Potential (ODP) of 0.7.

The case of  $\text{CH}_3\text{Br}$  is much more complex than the halons or indeed of any other potential ozone-depleting substance so far considered for regulation, because it is produced by the biosphere and is emitted into the atmosphere by natural processes. The atmospheric science of  $\text{CH}_3\text{Br}$  was reviewed in 1992 (Albritton and Watson, 1992) and many of the uncertainties associated with its atmospheric distribution, sources, sinks, and involve-

ment in the removal of ozone in the stratosphere were discussed. The present chapter is written against this background and the 1992 methyl bromide review will be referred to extensively (UNEP, 1992). A major objective of the present chapter will be to describe more recent progress towards defining a minimum and most likely ODP for  $\text{CH}_3\text{Br}$  and in highlighting the remaining uncertainties in our knowledge of its behavior in the atmosphere.

## 10.2 MEASUREMENTS, INCLUDING INTERHEMISPHERIC RATIOS

Methyl bromide is a ubiquitous component of the Earth's lower atmosphere. Over the past two decades, sporadic measurements have been made largely in the surface air but also in the free troposphere and stratosphere. These latter measurements have been performed using aircraft and balloon platforms. Here we provide a synthesis of much of the recently available data, with emphasis on the remote global atmosphere. In most cases, air samples are collected in pressurized stainless steel canisters and analyzed after a period of several days or weeks. In some instances, especially on shipboard platforms, this sampling process is omitted and the air sample is directly analyzed.

Many of the measurements have been made with a technique involving sample preconcentration (100-1000 ml), gas chromatographic separation, and electron capture detection. Other measurements have involved mass spectrometric detection; these are more specific and less prone to artifacts. Substantial uncertainties in absolute standards ( $\pm 30\%$ ) probably still exist but no systematic intercomparison studies have been performed to accurately quantify the level of uncertainty that is present in the published measurements. The reported mean concentrations fluctuate between 5-30 pptv, but there appears to be a convergence between 8-15 pptv in publications made since 1985. It is presumed that a large part of the differences in various measurements is due to the uncertainties in calibration standards. However, there is a distinct possibility that other sampling/analysis problems are also present, such as growth and decay in sample containers and co-elution of other substances with  $\text{CH}_3\text{Br}$  that are detected by the electron capture detector.

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**Table 10-1. Mean CH<sub>3</sub>Br mixing ratios (pptv) in the surface air of the Northern and Southern Hemispheres.**

NH	SH	NH/SH	Year	Platform (Region)	Latitude Range	Ref. No.
26	20	1.3	1981-1982 (December)	Ship (Pacific)	40°N - 32°S	(1)
15	11	1.4	1982-1983 (November)	Ship (Atlantic)	40°N - 75°S	(2)
11	10	1.2*	1985-1987 (Ann. Avg.)	Coastal (Pacific)	71°N - 44°S	(3)
11	8	1.4	1983-1992 (Ann. Avg.)	Coastal (Pacific)	71°N - 42°S	(4)
11	9	1.2	1992 (April/August)	Coastal (Pacific)	90°N - 45°S	(5)
12.0	9.5	1.3	1984-1993 (Spring/Fall)	Ship (Pacific, Atlantic)	60°N - 90°S	(6)

- (1) Singh *et al.* (1983)                      (2) Penkett *et al.* (1985)  
 (3) Cicerone *et al.* (1988)                  (4) Khalil *et al.* (1993)  
 (5) Blake *et al.* (1993)                      (6) Schauffler *et al.* (1993a); Schauffler, personal communication.  
 \* Note: the value of 1.15 has been corrected to 1.2 (Cicerone, 1994).

A number of campaigns have collected a body of data largely in the surface marine boundary layer in both hemispheres. In Table 10-1 we summarize the mean NH (Northern Hemisphere) and SH (Southern Hemisphere) surface air concentrations of CH<sub>3</sub>Br measured by several different investigators.

As stated earlier, most of the recent measurements show global mean concentrations in the vicinity of 8-15 pptv. In all cases a NH/SH gradient, which should be independent of calibration uncertainties, is observed. The higher NH mixing ratios have been ascribed to the domination of anthropogenic CH<sub>3</sub>Br sources in the NH (*e.g.*, Singh and Kanakidou, 1993; Reeves and Penkett, 1993). It is pertinent to note that the observed surface NH/SH gradients are by no means uniform and a range of 1.2 to 1.45 has been observed (Albritton and Watson, 1992). Figure 10-1 shows the variability that is inherent in an extensive marine air data set collected by one set of workers at different times and in different locations (Schauffler *et al.*, 1993a) and it probably reflects the spatial and temporal variability in the sources of CH<sub>3</sub>Br or, alternatively, it may reflect experimental artifacts. Another factor in the calculation of interhemispheric ratios from various data sets is the latitudinal range of the data.

This is sometimes restricted to a Southern Hemispheric limit of 40°S which, as can be seen from the Schauffler *et al.* data, would lead to a smaller ratio than a consideration of the full range of 60°N to 90°S. Overall the most likely value for the interhemispheric gradient is 1.3. This contrasts with the interhemispheric gradient for methyl chloride, which is close to 1 (Singh *et al.*, 1983) and strongly suggests a preponderance of Northern Hemispheric sources of CH<sub>3</sub>Br that are very possibly anthropogenic.

The major known removal process for CH<sub>3</sub>Br is its reaction with OH, resulting in an atmospheric lifetime of about 2 years. Theoretical studies suggest that such a chemical should show a distinct seasonal cycle larger than that observed for methyl chloroform, which would be expected to have a smaller amplitude. However, in a number of attempts so far, no distinct seasonal cycle has been observed (Singh *et al.*, 1983; Cicerone *et al.*, 1988; Khalil *et al.*, 1993). Figure 10-2 shows an example of this based on data collected in Tasmania and Oregon. Inadequate measurement precision, seasonal variations in the sources of CH<sub>3</sub>Br, or unidentified sinks may be responsible for a lack of observed seasonal behavior.

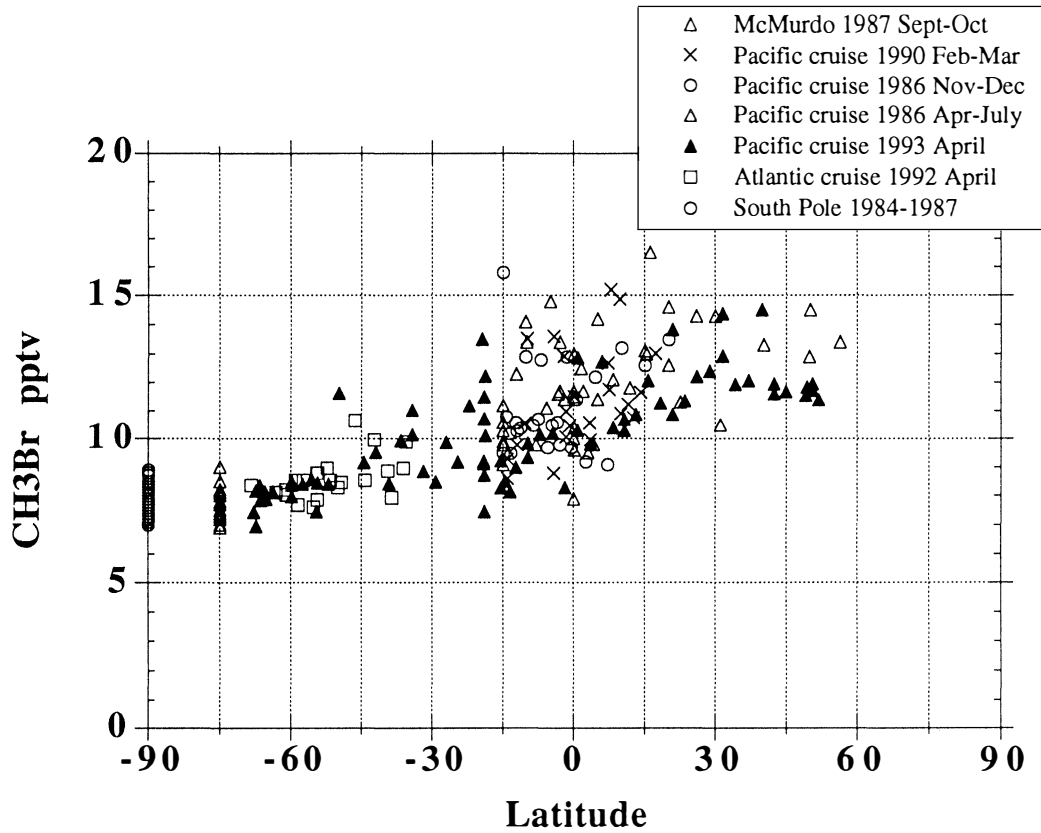


Figure 10-1. Latitudinal transect measurements of methyl bromide in oceanic air (after Schauffler *et al.*, 1993a; Schauffler, personal communication).

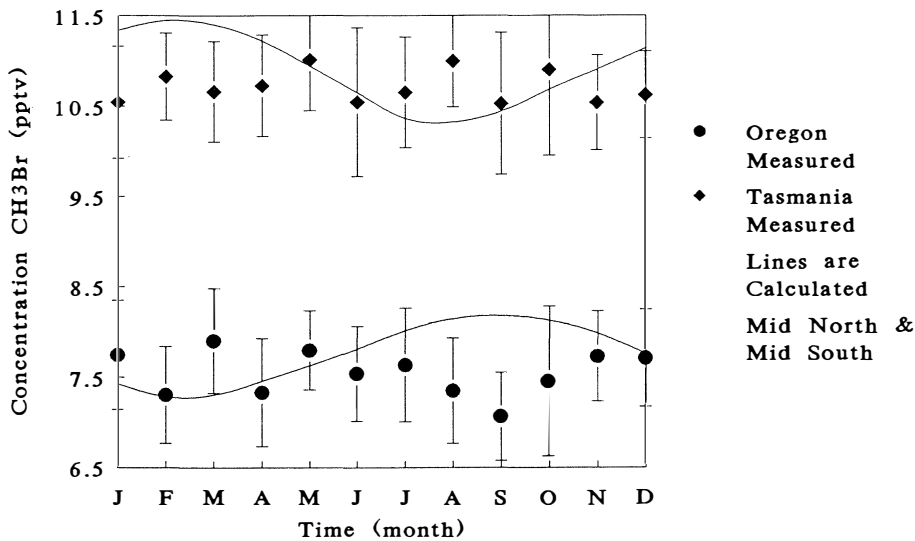


Figure 10-2. Seasonal cycle of methyl bromide in Tasmania (Southern Hemisphere) and Oregon (Northern Hemisphere). (After Khalil *et al.*, 1993.)

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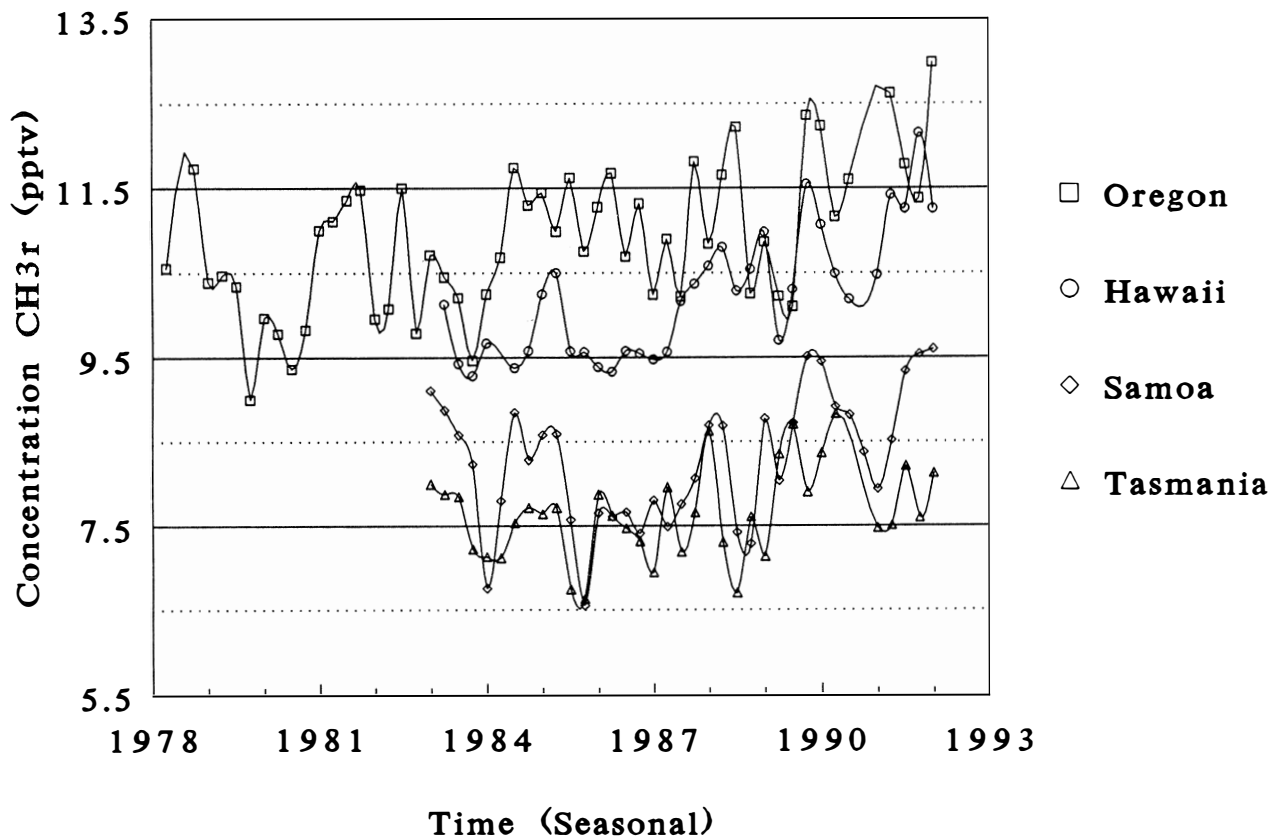


Figure 10-3. Trends in methyl bromide at four locations over the period 1978 to 1992. (After Khalil *et al.*, 1993.)

### 10.2.1 Vertical Profiles

The salient features of the vertical structure of CH<sub>3</sub>Br are that its concentrations decrease with increasing altitude at a slow rate in the troposphere (Blake *et al.*, 1993; Khalil *et al.*, 1993), and then relatively rapidly in the stratosphere (Lal *et al.*, 1994). The slight decrease in the troposphere is largely dictated by the surface source of CH<sub>3</sub>Br and a lifetime probably in excess of 1 year. The rapid loss in the lower stratosphere suggests strongly that CH<sub>3</sub>Br is a major source of bromine atoms in this region. Co-measurements of CH<sub>3</sub>Br and CFC-11 in the stratosphere by Schauffler *et al.* (1993b) will allow an accurate estimate of the stratospheric lifetime of CH<sub>3</sub>Br for ODP purposes.

### 10.2.2 Trends

Only one set of internally consistent data is available to assess atmospheric trends of CH<sub>3</sub>Br. Figure 10-3

shows the nature of data reported by Khalil *et al.* (1993) from four island sites in the NH and SH from 1978-1992. An evident feature is the large variability in these measurements that have no discernible seasonal character. Based on these data, Khalil *et al.* calculate a positive global trend of  $0.3 (\pm 0.1)$  pptv/year between 1988 and 1992 (Figure 10-3). It appears that a significant trend may not have existed prior to 1988. The positive trend in later years is not inconsistent with the mean trend of 0.2 pptv per year calculated from a consideration of increased agricultural usage (Singh and Kanakidou, 1993). However, these studies did not take into account changes that may have occurred in the potential source from gasoline consumption and the large biomass contribution. The variability in measured data is sufficiently large, and the data base sufficiently sparse, that a quantitative rate of increase cannot be reliably defined from these measurements alone. It is also likely that experimental artifacts associated with sample or standard storage would make

a small trend impossible to detect. Overall it can be concluded at present that no useful statement can be made from a consideration of the available trend data.

### 10.2.3 Calibration Issues

At the time of writing there has been no attempt to carry out an intercalibration exercise amongst the various groups making and publishing CH<sub>3</sub>Br measurements in the atmosphere. That such an exercise is clearly needed is shown by the data in Table 10-1. Accurate measurements of CH<sub>3</sub>Br will allow limits to be set on the source strength for comparison with independent estimates (see Section 10.3). They will also allow a data base to be built up in the future that could detect trends and seasonal variations, etc.

## 10.3 SOURCES OF METHYL BROMIDE

### 10.3.1 The Oceanic Source

The oceans are a major natural reservoir of bromine. They have generally also been regarded as a major natural source of atmospheric CH<sub>3</sub>Br, based principally on the measurements of Singh *et al.* (1983) that found surface water concentrations in the eastern Pacific Ocean to be 2.5 times the atmospheric equilibrium concentrations (*i.e.*, 150% supersaturation). From this value they calculated a net global oceanic source of about 300 Gg/yr. Singh and Kanakidou (1993) have recently revised this net flux estimate downward to 40-80 Gg/yr by correcting for large differences in calibration and by weighting the calculations according to regional ocean productivity differences. Taking only the correction for calibration differences and using a mean tropospheric mixing ratio of 11 pptv, together with the same air-sea exchange and solubility coefficients used by Butler (1994), yields a global net flux of about 110 Gg/yr for a supersaturation of 150%.

Most recently Khalil *et al.* (1993) have reported the results of CH<sub>3</sub>Br measurements from two Pacific Ocean expeditions in 1983 and 1987. They obtained a range of surface water saturations for these expeditions of 1.4 to 1.8 (*i.e.*, 40-80% supersaturation), and calculated a net global flux of 35 Gg/yr (range: 30-40 Gg/yr) by integrating the exchange fluxes as a function of latitude and ocean area, without allowing for latitudinal variations in the exchange coefficient or solubility. For

purposes of comparison, if one uses this measured mean supersaturation of 60%, together with the same 11 pptv mean tropospheric mixing ratio and the same air-sea exchange and solubility coefficients used by Butler, the resulting global net flux is 45 Gg/yr.

It is important to stress that these and other measurements of the air-sea disequilibrium of CH<sub>3</sub>Br can only be used to calculate net exchange fluxes across the air-sea interface. If, as is discussed below, the oceans are responsible for the chemical destruction of 50 Gg/yr of tropospheric CH<sub>3</sub>Br, then the global net oceanic fluxes reported above must be increased by this 50 Gg/yr to obtain gross strengths for the oceanic source. It is also important to stress that there is a very large uncertainty in the magnitude of the gross oceanic source, which is a necessary consequence of the disagreements among measurements of the air-sea disequilibrium and the uncertainties in the air-sea exchange rate and the oceanic chemical destruction rate. These are active research topics at the time of writing.

### 10.3.2 Agricultural Usage and Emission of CH<sub>3</sub>Br

The use of CH<sub>3</sub>Br for agricultural purposes was well covered in the UNEP 1992 Report (Albritton and Watson, 1992), and the respective table showing CH<sub>3</sub>Br sales over the period 1984-1990 is reproduced here with updated values for 1991 and 1992 provided by Duafala (personal communication, 1994) (Table 10-2). In 1990, 66.6 thousand tonnes were sold, with 3.7 thousand tonnes being used as a chemical intermediate (1 metric ton = 1 tonne = 10<sup>3</sup> kg). The resultant 63 thousand tonnes were used in the environment in some manner, with the amount in the column marked "Structural" referring to fumigation of buildings and containers, etc. All of this will escape to the atmosphere, but the fraction of the bulk of the CH<sub>3</sub>Br used for agricultural purposes that escapes is not known with any certainty. A theoretical analysis predicted that between 45 and 53% would do so, resulting in an atmospheric source from agricultural activities in the region of 30 thousand tonnes per year (Albritton and Watson, 1992).

An earlier analysis carried out in 1982 (Rolston and Glauz) compared measured concentrations of CH<sub>3</sub>Br in soil after application with those calculated by theory, with and without sheet covering at the time of injection. Theory and measurement agreed well with the



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Table 10-2. Methyl bromide sales, in thousands of tonnes.\*

Year	Pre-Planting	Post-Harvesting	Structural	Chemical Intermediates**	Total
1984	30.4	9.0	2.2	4.0	45.6
1985	34.0	7.5	2.3	4.5	48.3
1986	36.1	8.3	2.0	4.0	50.4
1987	41.3	8.7	2.9	2.7	55.6
1988	45.1	8.0	3.6	3.8	60.5
1989	47.5	8.9	3.6	2.5	62.5
1990	51.3	8.4	3.2	3.7	66.6
1991	55.1	10.3	1.8	4.1	71.2
1992	57.4	9.6	2.0	2.6	71.6

\* production by companies based in Japan, Western Europe, and the U.S.

\*\* not released into the atmosphere

assumption that most of the CH<sub>3</sub>Br escaped to the atmosphere, with 27% and 67% of the applied CH<sub>3</sub>Br escaping by 1 and 14 days, respectively, after fumigation. The work suggested that plastic barriers were almost totally ineffective in preventing CH<sub>3</sub>Br release in the long-term, but Rolston and Glauz appear to have used unusually permeable tarping material.

More recently, an experimental study was carried out by Yagi *et al.* (1993) to compare the flux of CH<sub>3</sub>Br released to the atmosphere with the amount applied. They showed that 87% was released to the atmosphere. Lower values have been obtained in unpublished studies conducted recently both by workers at the University of California at Davis and by Cicerone and co-workers, who found that application in wet soil conditions greatly reduced emissions to ~35%. Soil pH and organic matter parameters also influence rates of decomposition of CH<sub>3</sub>Br, and thus the fraction that escapes. Further, the depth and technique of injection are likely to exert some influence. To date, these factors have not been investigated thoroughly. Overall it is assumed here that 50% of the CH<sub>3</sub>Br used for purposes such as pre-planting and post-harvesting escapes to the atmosphere, leading to an emission in the region of 35 thousand tonnes per year in 1991 and 1992 from a usage of approximately 70 thousand tonnes per year for pre-planting, post-harvesting purposes, and structural purposes.

### 10.3.3 Biomass Burning

Recent measurements of gaseous emissions from biomass burning in very diverse ecosystems indicate that CH<sub>3</sub>Br is a significant combustion product (Manö and Andreae, 1994). In addition, satellite measurements suggest that biomass burning (*i.e.*, the burning of tropical, temperate, and boreal forests, savannas, grasslands, and agricultural lands following the harvest) is much more widespread and extensive than previously believed (Levine, 1991; Cahoon *et al.*, 1992; Andreae, 1993a). Almost all biomass burning is initiated or controlled by human activities, and pyrogenic emissions must therefore be classified as an anthropogenic source. Wildfires probably represent less than 10% of the biomass combusted globally (Andreae, 1993b). About 80% of biomass burning takes place in the tropics, mostly in conjunction with savanna fires, deforestation, and biomass fuel use. The emissions in the Southern Hemisphere, where the largest savanna areas are burned and most deforestation takes place, are about twice as large as those in the Northern Hemisphere (Andreae, 1993b; Hao *et al.*, 1990).

Measurements of CH<sub>3</sub>Br emissions were obtained from burning savanna grasslands in southern Africa and boreal forests in Siberia (Manö and Andreae, 1994), and from tropical forests in Brazil (Blake *et al.*, 1993). Manö and Andreae (1994) reported a CH<sub>3</sub>Br to CO<sub>2</sub> emission ratio from the south African savanna fires in the range of  $4.4 \times 10^{-8}$  to  $7.7 \times 10^{-7}$ , with an average of  $3.7 \times 10^{-7}$ .

(The emission ratio is the ratio of CH<sub>3</sub>Br in smoke minus ambient atmospheric CH<sub>3</sub>Br to CO<sub>2</sub> in smoke minus ambient atmospheric CO<sub>2</sub>.) The CH<sub>3</sub>Br to CO<sub>2</sub> emission ratios from the boreal forest fires in Siberia were higher, ranging from  $(1.1-13) \times 10^{-7}$ . The higher value from the boreal forest fire is probably due to the fact that forest fires usually have a lower combustion efficiency than grass fires and, hence, a larger fraction of the smoldering-phase compounds are produced. The emission ratio for CH<sub>3</sub>Br to methyl chloride (CH<sub>3</sub>Cl) from the south African and boreal forest fires was found to be about 1%, which is similar to the Br/Cl ratios found in plants (0.1-1%). Manö and Andreae (1994) have estimated the global emission of CH<sub>3</sub>Br from biomass burning based on the CH<sub>3</sub>Br to CO<sub>2</sub> and CH<sub>3</sub>Br to CH<sub>3</sub>Cl emission ratios. The global emission of CO<sub>2</sub> from biomass burning is in the range of 2.5-4.5 Pg C/yr (1 Petagram = 10<sup>15</sup> grams) and the global emission of CH<sub>3</sub>Cl from biomass burning is in the range of 0.65-2.6 Tg Cl/yr (1 Teragram = 10<sup>12</sup> grams) (Andreae, 1993b). Using these estimates of pyrogenic CO<sub>2</sub> and CH<sub>3</sub>Cl emissions and the corresponding CH<sub>3</sub>Br emission factors, Manö and Andreae (1994) estimate that the global production of CH<sub>3</sub>Br falls in the range from 9-37, and from 22-50 thousand tonnes CH<sub>3</sub>Br/yr, respectively. The range of emission from this source is thus 10-50 thousand tonnes per year, with perhaps a mid-range value of 30 thousand tonnes per year.

#### 10.3.4 Industrial Sources, including Gasoline Engine Exhaust

Methyl bromide is used as an intermediate compound in the manufacture of various industrial chemicals, including pesticides. Assessments for the preparation of the UNEP Methyl Bromide Technology Report, which is proceeding simultaneously with this report, suggest that approximately 2.1 thousand tonnes per year is emitted by inadvertent production and in the course of chemical processing.

Methyl bromide is also formed indirectly in the internal combustion engine from ethylene dibromide added in conjunction with lead tetraethyl to gasoline. According to a study conducted in 1989 (Baumann and Heumann), between 22 and 44% of the bromine in gasoline is emitted in an identified organic form in the exhaust, of which 64-82% is CH<sub>3</sub>Br.

Using these factors, an estimate for emissions of CH<sub>3</sub>Br from motor vehicle exhaust worldwide has been supplied for the year 1991-92 (M. Spiegelstein, personal communication, 1994). In this year about 24 thousand tonnes of ethylene dibromide were used in the U.S. and 37 thousand tonnes in the rest of the world, making a total of 61 thousand tonnes. This would allow a range of between 8.6 and 22 thousand tonnes of CH<sub>3</sub>Br to be emitted and a mean of 15 thousand tonnes.

The use of ethylene dibromide as a fuel additive has declined rapidly since the 1970s in the U.S. This is shown in Table 10-3.

In 1971, for instance, the amount of bromine used for gasoline additives in the U.S. was 121 thousand tonnes; this had declined to 100 thousand tonnes in 1978 and very rapidly thereafter down to 24 thousand tonnes in 1991. Obviously much more CH<sub>3</sub>Br would have been emitted from this source using the above analysis in the 1970s than in the 1980s, with at least 30 thousand tonnes being emitted from the U.S. alone in 1971. The decline in use of ethylene dibromide, however, has been compensated by the increase in use of bromine for a variety of other purposes, including flame retardants (specified) and most probably agricultural use of CH<sub>3</sub>Br, listed under "other," so that the total bromine usage has remained nearly constant (162 thousand tonnes in 1971 and 170 thousand tonnes in 1991). It is not impossible that the growth in emission to the atmosphere from agricultural usage could have compensated for the decline in emission from motor vehicle exhaust. No figures are available for the time dependence of gasoline usage of bromine in the rest of the world at the time of writing. Emission of CH<sub>3</sub>Br from this source is thus highly uncertain, but in the past it could have been dominant.

A recent study by the U.S. Environmental Protection Agency (W. Thomas, personal communication) estimates that between 10 and 30 tonnes of CH<sub>3</sub>Br were emitted from the 2 billion gallons of leaded gasoline used in 1992 in the United States. The same study estimated that about 100 billion gallons of leaded fuel are used worldwide. Assuming the same ethylene dibromide additive levels (0.04 gm per gallon) as in the United States, and the same emission factors as found by Baumann and Heumann, this would extrapolate to between 500 and 1500 tonnes of CH<sub>3</sub>Br emitted globally from this source. These numbers are probably low estimates, though, because the lead levels and hence

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**Table 10-3. U.S.: Bromine consumption by end-use, 1971 to 1991 (thousand tonnes).**

Year	Gasoline Additives	Sanitary Preparations	Flame Retardants	Other	Total
1971	121	11	16	14	162
1972	122	11	17	14	164
1973	115	17	27	6	165
1974	109	17	25	14	165
1975	100	17	22	16	155
1976	109	18	26	25	178
1977	103	18	29	20	170
1978	100	16	32	23	171
1979	91	26	28	35	180
1980	73	21	25	16	135
1981	54	26	35	35	150
1982	45	27	47	46	165
1983	39	16	45	48	148
1984	34	16	45	68	163
1985	35	-	52	85	172
1986	-	-	-	-	-
1987	30	14	41	67	152
1988	-	-	-	-	-
1989	32	24	49	70	175
1990	25	-	50	-	-
1991	24	9	48	89	170

[Source: Roskill Information Services Ltd., *The Economics of Bromine*, Sixth Edition, ISBN: 0 86214 383 7, London, 1992.]

ethylene dibromide levels used in gasoline in many countries are likely to be significantly larger than in the U.S.

To a large extent the discrepancy in emission of CH<sub>3</sub>Br from gasoline additives between the estimates is traceable to the quantities of ethylene dibromide assumed to be used in the U.S. Table 10-3, for instance, suggests that 24 thousand tonnes of bromine were being used in 1991, whereas the U.S. EPA Survey (W. Thomas, personal communication) estimated a usage of about 80 tonnes only.

### 10.3.5 Summary of CH<sub>3</sub>Br Emissions from Individual Sources

So far, four major sources and two minor sources have been identified for emission of CH<sub>3</sub>Br to the atmosphere. Table 10-4 gives a summary of the most likely

contribution made by each source, with ranges, to the atmospheric burden.

The uncertainty ranges in the estimates are also shown in Table 10-4, and they show the very imperfect state of knowledge with respect to sources of atmospheric CH<sub>3</sub>Br at the present time. In the case of the ocean, the newer, often unpublished, data indicate that it is an active sink, and thus zero net emission cannot be discounted. Agricultural emission estimates vary widely, mostly in association with the care taken and conditions prevailing at the time of application of the CH<sub>3</sub>Br. Biomass burning estimates are also very uncertain, reflecting the recent identification of this source and also current uncertainties in the magnitude of biomass burning sources of many compounds. The uncertainties in emission from structural purposes and those incurred during industrial processing are likely to be small, but the source of CH<sub>3</sub>Br associated with the inclusion of

**Table 10-4. Emission of CH<sub>3</sub>Br in thousand tonnes/year (best estimates).**

Source	Strength	Range	Anthropogenic	Natural
Ocean*	90	60 - 160	0	90
Agriculture	35	20 - 60	35	0
Biomass Burning	30	10 - 50	25	5
Gasoline Additives†	1	0.5 - 1.5	1	0
	15	9 - 22	15	0
Structural Purposes	4	4	4	0
Industrial Emissions	2	2	2	0
<b>Totals</b>	<b>162</b>	<b>97 - 278</b>	<b>67</b>	<b>95</b>
	<b>176</b>	<b>105 - 298</b>	<b>81</b>	<b>95</b>

\* The ocean source of 90 thousand tonnes per year is a gross source and is made up of two very uncertain quantities, as explained in Section 10.3.1, and the most likely value and the range are expected to change markedly as a result of new research.

† The two values given for this source reflect the large difference in the two estimates discussed in the text.

ethylene dibromide in leaded gasoline to prevent the accumulation of lead deposits in car engines could either be large or insignificant. Even given these uncertainties, however, it is very likely that the anthropogenic emissions make up at least 40% of the total. This percentage is heavily biased by the value given to the highly uncertain ocean source.

## 10.4 SINK MECHANISMS

The residence time of CH<sub>3</sub>Br in the Earth's atmosphere is controlled by various removal processes occurring in the atmosphere, in the oceans, and on land. The most quantitative information exists for tropospheric and stratospheric mechanisms involving chemical reaction and photolysis. However, there are several degradation processes that may be operative in oceanic surface waters. This is now an accepted removal process for CH<sub>3</sub>CCl<sub>3</sub> (Kaye *et al.*, 1994) and both the hydrolysis rate and the solubility of CH<sub>3</sub>Br are higher than those for CH<sub>3</sub>CCl<sub>3</sub>. Finally, a quantitative assessment of any global significance of the dry deposition of CH<sub>3</sub>Br on soils or vegetation is yet to be made.

### 10.4.1 Atmospheric Removal Processes

The removal of CH<sub>3</sub>Br within the atmosphere occurs primarily via its tropospheric reaction with the

hydroxyl radical (OH). The consistent body of laboratory data for this reaction (Mellouki *et al.*, 1992; Zhang *et al.*, 1992; Poulet, 1993) points to a tropospheric OH-removal lifetime for CH<sub>3</sub>Br of slightly greater than two years. Zhang *et al.* (1992) estimate a tropospheric lifetime with respect to OH of 2.1 years by a comparison with the OH reactivity of CH<sub>3</sub>CCl<sub>3</sub> (Talukdar *et al.*, 1992) coupled with the lifetime of the latter deduced from observational data (Prather, 1993). The use of the data from either of the other two kinetic studies yields the same value. Mellouki *et al.* (1992) used a coupled dynamical/chemical two-dimensional (2-D) model to calculate a tropospheric lifetime with respect to OH of 1.83 years. The OH reactive loss process for CH<sub>3</sub>Br is thought to dominate over reactions involving NO<sub>3</sub> or Cl. For example, tropospheric concentrations of NO<sub>3</sub> are highly variable, with nighttime values in continental air masses ranging from 20-200 pptv (Wayne *et al.*, 1991). Assuming an average nighttime concentration of 50 pptv over the continents in the lowest 2 km of the troposphere (with negligible concentrations during daytime and over the oceans), the lifetime for the removal of CH<sub>3</sub>Br by NO<sub>3</sub> is calculated to be greater than 28 years, using a comparative estimate for the reaction rate constant (Wayne *et al.*, 1991). Given the large uncertainty in this calculation and the small estimated contribution (~5%) to the tropospheric reactive lifetime, the NO<sub>3</sub> reaction will not be considered further in calculations of the over-

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**Table 10-5. Oceanic loss mechanisms for CH<sub>3</sub>Br.**

Process	Reaction	Loss Rate, % d <sup>-1</sup>	References
Neutral Hydrolysis	CH <sub>3</sub> Br + H <sub>2</sub> O → CH <sub>3</sub> OH + HBr	0.2 - 10	Elliott and Rowland (1993) Elliott (1984) Mabey and Mill (1978) Robertson <i>et al.</i> (1959) Laughton and Robertson (1956)
Basic Hydrolysis	CH <sub>3</sub> Br + OH <sup>-</sup> → CH <sub>3</sub> OH + Br <sup>-</sup>	< 1 - 10	Gentile <i>et al.</i> (1989) Mabey and Mill (1978) Fells and Moelwyn-Hughes (1959)
Nucleophilic Displacement	CH <sub>3</sub> Br + Cl <sup>-</sup> → CH <sub>3</sub> Cl + Br <sup>-</sup>	1 - 50	Elliott and Rowland (1993) Elliott (1984) Swain and Scott (1953)
UV Photosensitization	CH <sub>3</sub> Br + hν → (CH <sub>3</sub> Br) <sup>‡</sup> (CH <sub>3</sub> Br) <sup>‡</sup> + H <sub>2</sub> O → CH <sub>3</sub> OH + HBr	≤ 6 times neutral hydrolysis	Gentile <i>et al.</i> (1989) Castro and Belser (1981)
Biological Consumption	Uncertain	Uncertain	Rasche <i>et al.</i> (1990)

all lifetime. For the possible removal by atomic chlorine, the lifetime is even more difficult to estimate since there are no direct measurements of Cl in the troposphere and a mechanism for maintaining concentrations sufficient to have a significant impact ( $\sim 10^5 \text{ cm}^{-3}$ ) on a global scale is not known. In fact, model calculations support much lower global tropospheric Cl concentrations, on the order of  $10^2 - 10^3 \text{ cm}^{-3}$ , yielding Cl removal lifetimes for CH<sub>3</sub>Br of 750 - 7500 years. A minor, but clearly identified, removal process occurring in the atmosphere involves the transport of CH<sub>3</sub>Br to the stratosphere followed by its reaction with OH and photodissociation, with a lifetime of approximately 35 years (Prather, 1993). Therefore, the overall lifetime of CH<sub>3</sub>Br associated with identified atmospheric removal processes alone is approximately 2 years with an overall uncertainty of  $\pm 25\%$ .

### 10.4.2 Oceanic Removal Processes

There is growing evidence that CH<sub>3</sub>Br is destroyed in seawater by up to five processes of differing

efficiencies (Table 10-5). Three of these have been investigated to some extent in pure water and seawater, allowing for rough estimates of the degradation rate of CH<sub>3</sub>Br in the surface ocean (Table 10-5).

According to Elliott and Rowland (1993) the predominant reaction in seawater is chloride substitution, which is significantly more effective than hydrolysis. They further suggest that these reactions could be a factor of 10 times faster or slower at the oceanographic extremes of 0°C and 30°C. The other two mechanisms (photosensitization by ultraviolet light and destruction by microorganisms) have not been studied under conditions representative of natural systems, thereby not permitting quantification of these rates at the present time. However, there is a limit to the effect that aquatic degradation can have on the atmospheric flux, since at high loss rates, the flux will be restricted by air-sea exchange, as discussed in Section 10.5. These data can be used to compute an area-weighted removal rate for CH<sub>3</sub>Br in seawater of 10% per day (J. Butler, private communication) with a probable range of 3-30% d<sup>-1</sup>, de-

pending on the actual rates and their dependencies on salinity, temperature, and (in the case of biological losses) oceanic productivity. It must be stressed here, however, that the ocean loss process has not been investigated with the same thoroughness as the homogeneous gas phase loss processes discussed above, and that the absolute magnitude of this process is therefore not well defined at present. The impact of oceanic loss of  $\text{CH}_3\text{Br}$  on the overall atmospheric lifetime is discussed later in Sections 10.5 and 10.8.

#### 10.4.3 Surface Removal Processes

Recent experiments have indicated the potential for degradation of  $\text{CH}_3\text{Br}$  in different environments. Anaerobic degradation in salt marsh sediments (Oremland *et al.*, 1994b), has been attributed to nucleophilic substitution reactions with sulfides of biological origin. Time constants of 2-5 days for  $\text{CH}_3\text{Br}$  consumption were measured. Laboratory and field experiments have also provided evidence for biodegradation by methanotrophic bacteria (Oremland *et al.*, 1994a), with time constants of a day or less. However, the degradation time constant seems to be inversely related to the relative concentrations of  $\text{CH}_4$  and  $\text{CH}_3\text{Br}$  in the experiments. Because the smallest initial concentrations of  $\text{CH}_3\text{Br}$  injected in these studies were of the order of ppmv, it is difficult to extrapolate time constants to the pptv levels typical of the atmosphere. Other soil types may also consume  $\text{CH}_3\text{Br}$ ; in the soil,  $\text{CH}_3\text{Br}$  will be partitioned between soil gas, liquid, and solid phases. The effectiveness of soil sinks would depend on (a) the rate of consumption by physical and/or biological processes in the soil, and (b) the rate of exchange of soil gas with the overlying atmosphere. Experiments to evaluate these processes should be performed with  $\text{CH}_3\text{Br}$  concentrations as close as possible to those in the ambient atmosphere because, for example, soil microbes may exhibit different activities in different concentration ranges.

Given the lack of information on any of the individual processes involved, further laboratory and field measurements are required to quantify the role of any land uptake and degradation of  $\text{CH}_3\text{Br}$ , and it is not included further in atmospheric lifetime calculations.

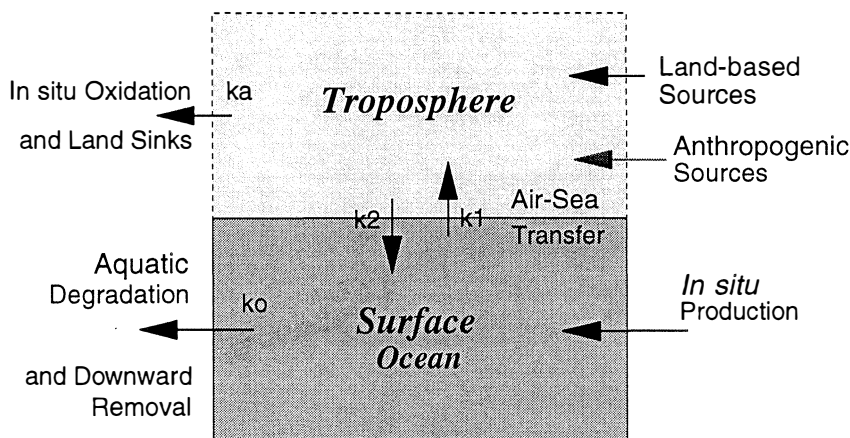
### 10.5 THE ROLE OF THE OCEANS

The oceans represent an important special case in the global tropospheric budget of  $\text{CH}_3\text{Br}$ . As indicated previously, the oceans are not only likely to be the largest natural source of tropospheric  $\text{CH}_3\text{Br}$ , they have at the same time been shown to be an important natural sink of tropospheric  $\text{CH}_3\text{Br}$  through chemical removal processes in the oceanic mixed layer. Because the exchange time of tropospheric  $\text{CH}_3\text{Br}$  with the surface layer of the ocean is of the same order of magnitude as its tropospheric residence time with respect to photochemical destruction, its time-dependent response must be evaluated in the context of a coupled ocean-atmosphere system.

Butler (1994) was the first to draw attention to the relationships between the oceanic production and loss mechanisms for  $\text{CH}_3\text{Br}$  and the tropospheric lifetime of  $\text{CH}_3\text{Br}$ . To illustrate these relationships, we present here a much-simplified tutorial that leans heavily on the work of Butler and qualitatively and quantitatively reproduces the main characteristics of the coupled ocean-atmosphere system. In our subsequent assessment of the effect of the oceans on the atmospheric  $\text{CH}_3\text{Br}$  lifetime and its effect on the Ozone Depletion Potential, we rely on Butler's (1994) published values.

#### 10.5.1 A Simple Ocean-Atmosphere Model

Consider a simple two-box model representing the average square meter of ocean surface (Figure 10-4). Above this surface the equivalent volume of atmosphere, calculated by dividing by the fraction of the Earth's surface that is covered by ocean (0.71), corresponds to a column height of 11.9 km calculated at 20°C and 1 atm. The mean depth of the oceanic mixed layer below this surface is taken as 75 m, but because the volume equilibrium partition coefficient (*i.e.*, the Ostwald solubility coefficient, *S*) favors the liquid phase by a factor of 3.9 at 20°C (Singh *et al.*, 1983), the equivalent depth of the mixed layer reservoir with respect to atmospheric  $\text{CH}_3\text{Br}$  is  $3.9 \times 75 \text{ m} = 293 \text{ m}$ . Here we have used the same mixed layer depth as Butler (1994), but we have done the calculation for a mean solubility at 20°C rather than the value at 25°C used by Butler. The effects of this difference and other minor differences in the calculations are discussed below.

Two-Box Model for Atmospheric CH<sub>3</sub>Br

**Figure 10-4.** A two-box model illustrating methyl bromide coupling between atmosphere and ocean (after Butler, 1994).

In this simple system the effective volumes of the two reservoirs for CH<sub>3</sub>Br differ by a ratio of  $11,900 \div 293 = 41$ . That is, when the ocean mixed layer is at solubility equilibrium with the atmosphere, only about 2.5% of the atmospheric burden resides in the mixed layer. The magnitude of “buffering” of the atmospheric burden of CH<sub>3</sub>Br by the additional CH<sub>3</sub>Br in ocean surface waters is therefore realistically limited to only about 2 or 3 percent.

Butler (1994) estimates that the mean atmospheric exchange coefficient, or “piston velocity,” for dissolved oceanic CH<sub>3</sub>Br is about 4.1 m/d. That is, for a 75 m mixed layer, the CH<sub>3</sub>Br mean residence time with respect to atmospheric exchange is  $(75 \text{ m}) \div (4.1 \text{ m/d}) = 18.3 \text{ d}$ . As the exchange flux must be equal in both directions and the atmospheric reservoir is 41 times larger than the mixed layer reservoir, the residence time of atmospheric CH<sub>3</sub>Br with respect to oceanic exchange is  $41 \times 18.3 \text{ d} = 750 \text{ d}$ , or 2.1 years.

The mean residence time of dissolved CH<sub>3</sub>Br in the oceanic mixed layer with respect to the various chemical destruction mechanisms listed in Table 10-5 has been estimated by Butler (1994) at about 10 d. For purposes of illustration, consider first how the simple two-box model would behave if the chemical destruction rate in the surface ocean were infinite. In this case the mixed layer concentration would be zero, and the up-

ward component of the exchange flux would be reduced to zero while the downward component would remain unchanged. Thus, the atmospheric residence time with respect to oceanic exchange of 2.1 years would also be the atmospheric lifetime with respect to oceanic chemical destruction, and the air-sea exchange rate would become the rate-limiting step. In other words, within the uncertainties in the air-sea exchange rate, the atmospheric lifetime with respect to oceanic chemical destruction cannot be less than 2.1 years.

Consider now the balance that is achieved for CH<sub>3</sub>Br in the oceanic mixed layer if the mean replacement time by atmospheric exchange is 18.3 d, the mean chemical destruction lifetime is 10 d, and there is no oceanic production. If  $f$  is the fraction of the equilibrium atmospheric CH<sub>3</sub>Br concentration in the mixed layer at steady state, then the atmospheric replacement rate, which is proportional to  $(1-f) \div 18.3 \text{ d}$ , must be equal to the destruction rate, which is similarly proportional to  $f \div 10 \text{ d}$ . Solving for  $f$  gives a value of 0.35. That is, for the given ratio of the air-sea exchange and chemical destruction rate constants, and no oceanic production, the mixed layer will be 65% undersaturated with respect to atmospheric equilibrium. The corresponding atmospheric CH<sub>3</sub>Br lifetime with respect to oceanic chemical destruction then becomes  $2.1 \text{ y} \div 0.65$ , or 3.2 years.

It is important to recognize that this 3.2-year atmospheric lifetime of  $\text{CH}_3\text{Br}$  with respect to oceanic removal does not depend on whether the oceans are a net source or sink for the atmosphere. This is because air-sea exchange and oceanic chemical destruction are both regarded as first-order processes. Any  $\text{CH}_3\text{Br}$  production in the oceans will be partly destroyed *in situ* and partly exchanged with the atmosphere, where it will be subjected to the same combination of atmospheric and oceanic losses as  $\text{CH}_3\text{Br}$  produced elsewhere, either naturally or anthropogenically.

### 10.5.2 Oceanic Uptake and the Atmospheric Lifetime

Butler (1994) carried out calculations similar to the above tutorial, except that he included a relatively small term for mixing between the oceanic mixed layer and the underlying waters. The greatest difference between the two calculations is that Butler used the mean solubility coefficient at 25°C rather than 20°C, which leads to an increase of about 20% in the calculated atmospheric lifetime with respect to oceanic destruction. Although the mean ocean surface temperature is about 18°C, there is reason to weight the calculation toward the higher temperature solubilities because the chemical removal rates are much greater in warmer waters. Finally, neither calculation takes into account that only the ~85% of the atmosphere that is in the troposphere is able to exchange with the oceans on this time scale. Correction for this effect would shorten the atmospheric lifetime with respect to oceanic destruction by about 15% in both calculations.

Using the results reported by Butler (1994), the best atmospheric mean lifetime for  $\text{CH}_3\text{Br}$  with respect to oceanic destruction is 3.7 years, with a large uncertainty range of 1.3 to 14 years that depends principally on the large uncertainties in the aquatic degradation rate and the air-sea exchange rate. Assuming a mean tropospheric  $\text{CH}_3\text{Br}$  mixing ratio of 11 pptv, this corresponds to an oceanic destruction of about 50 Gg/yr (range: 136 - 13 Gg/yr). If the atmospheric lifetime with respect to atmospheric photochemical destruction alone is 2.0 years, then the corresponding best combined lifetime is 1.3 years (range: 0.8 - 1.7 years).

## 10.6 MODELED ESTIMATES OF THE GLOBAL BUDGET

### 10.6.1 Introduction

In recent years, there have been several attempts to determine the strength of the anthropogenic  $\text{CH}_3\text{Br}$  source by constraining model calculations with observed atmospheric concentrations. These model calculations have varied from 3-D and 2-D models to simple 2-box models, but the principle, intrinsic to all these model studies, has been to investigate the latitudinal gradient exhibited in the observations and to account for the magnitude of the average mixing ratio. The results of these studies are summarized in Table 10-6. The atmospheric lifetime of  $\text{CH}_3\text{Br}$ , required for these studies, has largely been estimated by combining modeled OH fields with reaction kinetic data derived from laboratory studies, and the individual lifetimes shown in the table reflect differences in these quantities at the times of publication of the modeling studies. This has the advantage, however, of considering a range of lifetimes including those from gas phase processes alone and including both atmospheric and oceanic removal. None of the modeling studies referred to here explicitly considered sources such as biomass burning and motor vehicle exhausts or a substantial ocean sink. Even so, conclusions concerning the proportions of source type between natural and anthropogenic and the overall annual budget are probably valid.

### 10.6.2 Budget and the Anthropogenic Contribution

Singh and Kanakidou (1993) used a simple model made up of 2 boxes, each representing a hemisphere, with an interhemispheric exchange rate of 1.1-1.2 years. Assuming a lifetime of 1.7-1.9 years, no natural sources, and injecting 93% of the anthropogenic emissions into the Northern Hemispheric box, an interhemispheric N/S ratio of 1.6-1.8 was calculated. Their 2-D model also produced a similarly high interhemispheric ratio. The 2-D model of Reeves and Penkett (1993), calculates the interhemispheric ratio of the surface concentrations to be 1.69 when no natural sources are assumed and all anthropogenic emissions are injected into the northern midlatitudes (see Figure 10-5 for their relationship between the interhemispheric ratio and anthropogenic



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**Table 10-6. Modeled atmospheric CH<sub>3</sub>Br.**

Reference	Model	Lifetime (yr)	Source (ktonnes yr <sup>-1</sup> )	Atmos. Burden <sup>c</sup> (ktonnes)	Average Conc. (pptv)	Anthro- pogenic %	N/S ratio
Singh and Kanakidou (1993)	2-box	1.7-1.9	–	167.4	–	100	1.6-1.8
		1.7-1.9	93	167.4	12	35 (20-50)	1.1-1.25
		1.2	147	176.4	12	27 (20-35)	1.1-1.25
Khalil <i>et al.</i> (1993)	4-box	2.0	96	150.0	9.3	30-70 <sup>b</sup>	1.34
Singh and Kanakidou (1993)	2-D	1.9	72	136.8	–	100	1.37 <sup>a</sup>
		1.9	84	159.6	11 <sup>a</sup>	29	1.08 <sup>a</sup>
		1.2	84	100.8	6-7 <sup>a</sup>	29	1.18 <sup>a</sup>
Reeves and Penkett (1993)	2-D	1.78	91	162.0	11	100	1.69
		1.78	91	162.0	11	54 (33-74)	1.3±0.15
		1.78	91	162.0	11	25-48	1.1-1.25
Prather (Albritton and Watson, 1992)	3-D	2.0	100	200.0	12.5	100	>2.0
		2.0	100	200.0	12.5	25 (13-40)	1.3±0.15
		1.0	200	200.0	12.5	6-20	1.3±0.15

Results given for 2- and 4-box models as tropospheric column averages and for the multi-dimensional models as lowest layer averages, unless stated otherwise.

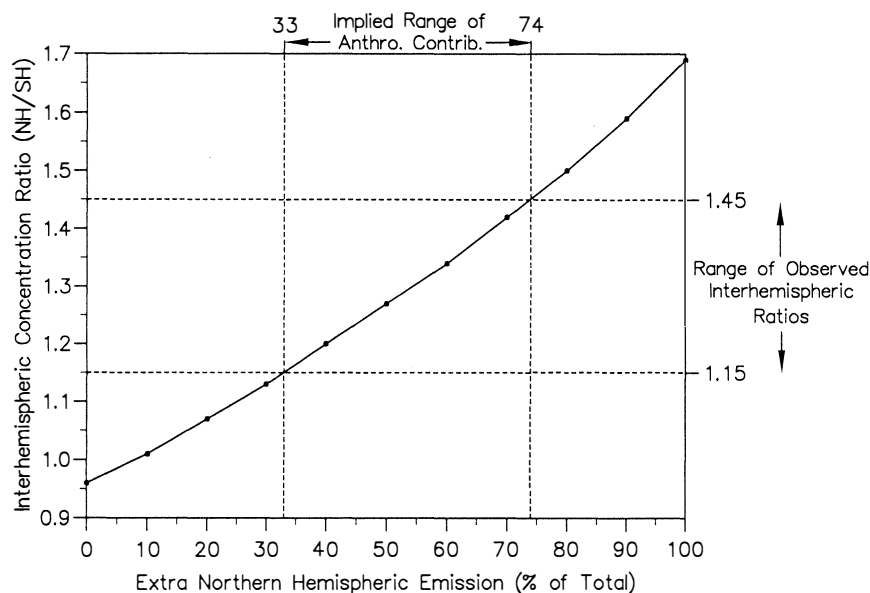
- a Tropospheric column average.
- b Includes unknown source in the tropics, possibly biomass burning, which amounts to up to 30% of the total source.
- c Calculated assuming steady state, *i.e.*, production × lifetime

contribution to atmospheric CH<sub>3</sub>Br). Prather (Albritton and Watson, 1992), using a 3-D model, calculated an interhemispheric ratio greater than 2 when all emissions were released in the Northern Hemisphere and a lifetime of 2 years was assumed.

Some caution must be shown when comparing the results of these modeling studies (Table 10-6), since there are several inherent differences in the various simulations. For example, each box of the 2-box model represents the tropospheric average, whilst the results from the lowest layer are quoted for the 2-D models. Both the 2-D models indicate a slight decrease in interhemispheric ratio with increasing altitude (*e.g.*, a ratio of 1.3 at 0-2.5 km, decreasing to 1.2 at 7.5-10 km [Reeves and Penkett, 1993]). Consequently, the interhemispheric ratio of the tropospheric averages should be lower than that of the surface averages. Another difference is the latitudinal and, in the case of the 3-D model, the longitudinal distribution of the emissions within the Northern Hemisphere.

Despite these differences, it is clear that the inter-hemispheric ratios, calculated by all these models for a Northern Hemispheric, presumably anthropogenic source, are considerably higher than the observed surface ratio of  $1.3 \pm 0.15$  (Albritton and Watson, 1992). This indicates the existence of a source releasing CH<sub>3</sub>Br, at least in part, into the Southern Hemispheric atmosphere, which could be oceanic or biomass burning according to the discussion of sources in Section 10.3.

Both Reeves and Penkett (1993) and Singh and Kanakidou (1993) then, by analogy to methyl chloride (CH<sub>3</sub>Cl), assumed an evenly distributed natural source of CH<sub>3</sub>Br. Reeves and Penkett (1993) were best able to fit their model results to the  $1.3 \pm 0.15$  observed surface ratio when the extra Northern Hemispheric contribution was 54% (33-74%) of the total source (see Figure 10-5). Singh and Kanakidou (1993) present 2-D results for which the extra Northern Hemispheric contribution was 29% of the total.



**Figure 10-5.** Relationship between the extra Northern Hemispheric source contribution and the interhemispheric ratio, as calculated in a 2-D global model (after Reeves and Penkett, 1993).

The 3-D modeling work of Prather (Albritton and Watson, 1992) suggests that the observed concentrations and interhemispheric ratio could be explained by an emission rate 25 (13-40) thousand tonnes  $\text{yr}^{-1}$  greater in the Northern Hemisphere, with a total source strength of about 100 thousand tonnes  $\text{yr}^{-1}$ . This implies an anthropogenic contribution of 25% (13-40%) of the total emissions.

Khalil *et al.* (1993) employed a 4-box model to analyze their observed  $\text{CH}_3\text{Br}$  concentrations. Each box was of equal volume,  $0^\circ$ - $30^\circ$  and  $30^\circ$ - $90^\circ$  in each hemisphere, with intrahemispheric transfer rates of 0.25 years and an interhemispheric rate of 0.55 years giving a total transport time across all latitudes of 1.05 years. By carrying out a budget analysis in each region, they deduced that 60% of  $\text{CH}_3\text{Br}$  emissions occur in the tropical regions, with the rest mostly from the middle-to-high northern latitudes. They also concluded that the total emissions are around 100 thousand tonnes  $\text{yr}^{-1}$  and that the ratio of emissions between the Northern and Southern Hemispheres is between 2 and 4. From their results they conclude that the anthropogenic source is at least 30 thousand tonnes  $\text{yr}^{-1}$ , and based on their calculated oceanic source of 30-40 thousand tonnes  $\text{yr}^{-1}$ , of which 25 thousand tonnes  $\text{yr}^{-1}$  is in the tropics, they identified an

unexplained tropical source. If this is biomass burning, the total anthropogenic contribution will be 60-70 thousand tonnes  $\text{yr}^{-1}$  (see Table 10-4).

Employing a lifetime of 1.2 years to account for deposition to the ocean, Singh and Kanakidou's 2-box model results in an extra Northern Hemisphere fraction of 27% (20-35%), whilst the interhemispheric ratio of their 2-D model increased by about 15%. Using a lifetime of 1 year for  $\text{CH}_3\text{Br}$  in the 3-D model, Prather calculated a total emission source of 200 thousand tonnes  $\text{yr}^{-1}$ , with an extra Northern Hemispheric contribution of 6-20%.

Table 10-6 also shows the atmospheric  $\text{CH}_3\text{Br}$  burden for each of the model runs reported. These have been calculated as the production (emission) rate multiplied by the lifetime, assuming steady state. Considering those runs that attempted to reproduce realistic average concentrations, the atmospheric burden varies from 160-200 thousand tonnes, with an average of 177 thousand tonnes. Linking this burden with the maximum source allowed by Table 10-4 would produce a minimum atmospheric lifetime of 0.6 years for  $\text{CH}_3\text{Br}$  due to all sink processes.

## Inorganic Bromine Cycling

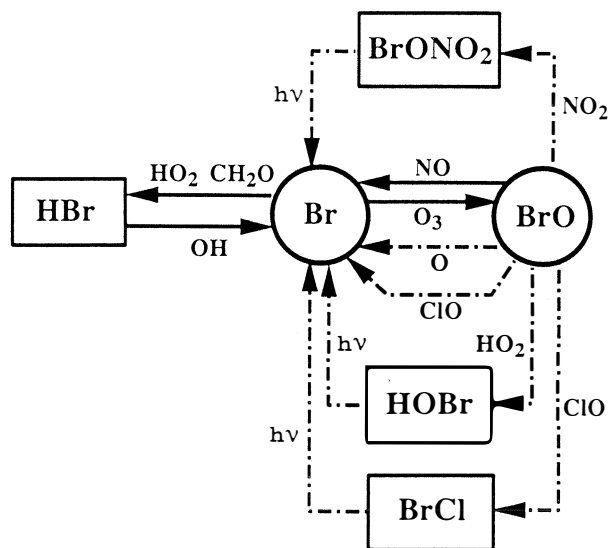


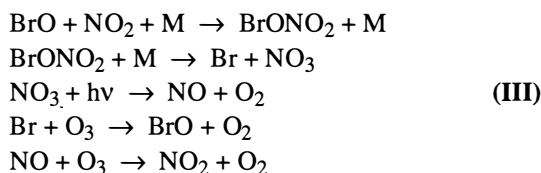
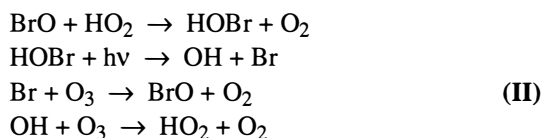
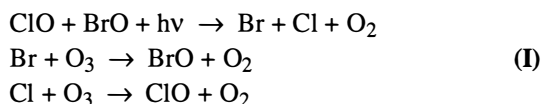
Figure 10-6. Stratospheric gas phase bromine cycle.

### 10.7 STRATOSPHERIC CHEMISTRY: MEASUREMENTS AND MODELS

The chemistry of bromine in the stratosphere is analogous to that of chlorine and is shown schematically in Figure 10-6. Upon reaching the stratosphere, the organic source gases photolyze or react with OH and O(<sup>1</sup>D) rapidly to liberate bromine atoms. Subsequent reactions, predominantly with O<sub>3</sub>, OH, HO<sub>2</sub>, ClO, NO, and NO<sub>2</sub>, partition inorganic bromine between reactive forms (Br and BrO) and reservoir forms (BrONO<sub>2</sub>, BrCl, HOBr, and HBr). However, unlike chlorine chemistry, where reactive forms are a small fraction of the total inorganic budget (except in the highly perturbed polar regions in wintertime), reactive bromine is about half of the total inorganic bromine budget in the lower stratosphere. Therefore, bromine is more efficient in catalytic destruction of ozone than is chlorine. In addition, the gas phase photochemical partitioning between reactive and reservoir forms of bromine is fairly rapid in sunlight, on the order of an hour or less, such that direct heterogeneous conversion of HBr and BrONO<sub>2</sub> to BrO is likely to have little impact on the partitioning of bromine, except perhaps in polar twilight (see later).

Mixing ratios of NO<sub>x</sub>, HO<sub>x</sub>, and ClO<sub>x</sub> increase more strongly with altitude above 20 km than does BrO,

and the fractional contribution to ozone loss due to bromine is greatest in the lower stratosphere (Avallone *et al.*, 1993a; Garcia and Solomon, 1994). There, where oxygen atom concentrations are small, the O + BrO reaction is relatively unimportant, and the three reaction cycles listed below are primarily responsible for bromine-catalyzed ozone loss, with Cycle III being of less importance than Cycles I and II:



In the polar regions, where NO<sub>x</sub> is reduced and ClO is enhanced by heterogeneous reactions on sulfate aerosols and polar stratospheric clouds, Cycle I dominates the ozone loss due to bromine. At midlatitudes the first two cycles contribute approximately equally to ozone loss at 20 km, and Cycle II is the most important near the tropopause, where the abundance of HO<sub>2</sub> is substantial but where ClO abundances are negligible.

#### 10.7.1 Observations

Measurements of organic bromine across the tropopause indicate that mixing ratios of total bromine in the stratosphere should be about 18 pptv, with CH<sub>3</sub>Br providing 54% (Schauffler *et al.*, 1993c). Both remote and *in situ* measurements of BrO indicate mixing ratios are between 4 and 10 pptv, generally increasing with altitude, in the lower stratosphere (Brune *et al.*, 1990; Carroll *et al.*, 1990; Toohey *et al.*, 1990; Wahner *et al.*, 1990; Wahner and Schiller, 1992; Arpag *et al.*, 1994). Results from photochemical models are in good agreement with *in situ* BrO profiles between 16 and 22 km (Garcia and Solomon, 1994). However, profile information above 22 km is limited because all *in situ* data to

date have been obtained with the NASA ER-2 aircraft, a platform with an altitude ceiling of 22 km, and it is difficult to derive profile information above 20 km from column measurements (Arpag *et al.*, 1994).

Attempts to observe HBr directly by far-infrared emission techniques have been hampered by the small anticipated abundances, especially at high altitudes where these techniques are most sensitive (Traub *et al.*, 1992). However, a systematic search of dozens of individual spectra obtained at various altitudes from about 25 km to 35 km revealed a small positive signal that could be attributed to an average HBr mixing ratio of about 1 pptv of HBr (Traub 1993). Within the measurement uncertainties, these observations are broadly consistent with results from photochemical models that include a small HBr branching ratio (less than 5%) for the  $\text{BrO} + \text{HO}_2$  reaction and show no unexpected features, suggesting that the major sources of HBr have been accounted for adequately in ozone loss calculations. Supporting these observations are results from a 2-D model (Garcia and Solomon, 1994) indicating that an HBr yield of greater than a few percent is also not consistent with the *in situ* observations of the abundances and latitudinal gradient of BrO at midlatitudes. Thus, HBr likely represents a minor reservoir for reactive bromine in the lower stratosphere and is unlikely to exceed 2% of total bromine.

Information about inorganic bromine photochemistry is available from geographic and solar zenith angle variations in BrO. Mixing ratios within the polar vortices are about twice as great as values observed at midlatitudes under background sulfate aerosol conditions, consistent with the differences in  $\text{NO}_x$  abundances in these regions (Toohey *et al.*, 1990). Higher BrO abundances observed at midlatitudes following the eruption of Mount Pinatubo (Avallone and Toohey, 1993; Arpag *et al.*, 1994) reflected the concurrent decreases in  $\text{NO}_x$  due to enhanced heterogeneous reaction of  $\text{N}_2\text{O}_5$  on sulfate aerosols. Similar increases were observed in ClO (Avallone *et al.*, 1993b). The results of ER-2 diurnal studies (Toohey *et al.*, 1990) and remote observations at sunrise and sunset of both BrO and OCIO (Solomon *et al.*, 1990; Arpag *et al.*, 1994), the latter a by-product of the ClO and BrO reaction, indicate that reactive bromine is tied up at night into photolytically labile reservoir forms such as  $\text{BrONO}_2$  and  $\text{BrCl}$ . These results are consistent with inferences that  $\text{BrONO}_2$  is a major inorganic

bromine reservoir. However, some measurements from the NASA DC-8 aircraft at northern high latitudes reveal non-zero BrO column abundances in darkness that cannot be explained with standard photochemistry (Wahner and Schiller, 1992).

### 10.7.2 Laboratory Studies

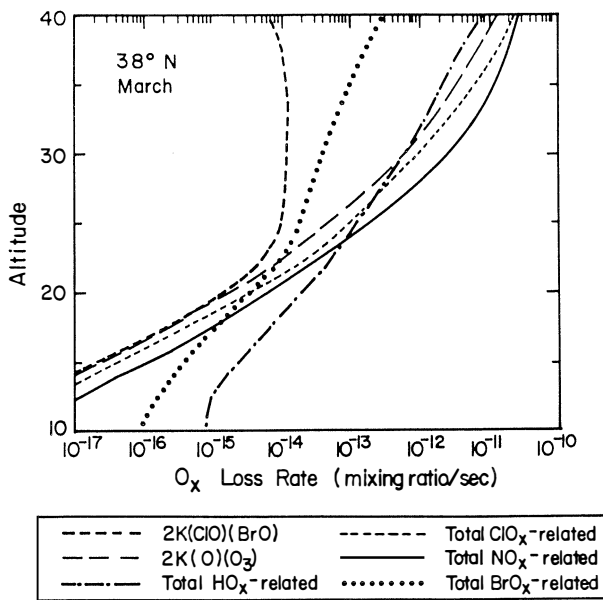
A breakdown of the contributions from the catalytic cycles above indicates that Cycle I and Cycle II account for most of the bromine-catalyzed ozone loss and contribute about equally (Isaksen, 1993). At lower altitudes, where bromine reactions contribute most to ozone loss rates and the alpha factor is greatest (Garcia and Solomon, 1994), temperatures are low (below 220K) and there are some uncertainties in BrO kinetics. The reaction between BrO and ClO is complex, but it has been studied extensively under stratospheric conditions and appears to be well understood (DeMore *et al.*, 1992). Remote observations of BrO and OCIO, the latter produced by the side reaction  $\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{OCIO}$  and itself not affecting ozone, and diurnal studies of BrO *in situ* support the view that our understanding of the coupled photochemistry between BrO and ClO is basically sound at stratospheric pressures and temperatures (Solomon *et al.*, 1990; Wahner and Schiller, 1992).

Recent measurements of the rate constant for the BrO and  $\text{HO}_2$  reaction indicate that at room temperature it is about six times larger than previously reported, making Cycle II correspondingly more efficient (Poulet *et al.*, 1992; Bridier *et al.*, 1993; Maguin *et al.*, 1994). Furthermore, it is now clear that the major reaction products are HOBr and  $\text{O}_2$ . A recent report of the upper limit to the efficiency of the channel yielding  $\text{HBr} + \text{O}_3$  at room temperature gave a value of less than 0.01% (Mellouki *et al.*, 1994), which was established by investigating the rate of the reverse reaction, namely,  $\text{HBr} + \text{O}_3 \rightarrow \text{BrO} + \text{HO}_2$ . A direct determination at stratospheric temperatures remains to be carried out.

### 10.7.3 Ozone Loss Rates

Loss rates of ozone as calculated by a photochemical model that best reproduces observations of ozone,  $\text{NO}_x$ , ClO, and BrO obtained at midlatitudes at the spring equinox appear in Figure 10-7 (Garcia and Solomon, 1994). Because bromine is released more rapidly with altitude than chlorine, and because a greater

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**Figure 10-7.** Midlatitude ozone loss rates associated with various removal cycles between 15 and 30 km (after Garcia and Solomon, 1994).

fraction of inorganic bromine remains in active forms, catalytic destruction of ozone by bromine is more important than chlorine on a mole-per-mole basis. As a consequence, at about 20 km the bromine contribution to the overall ozone loss rate is nearly as important as the chlorine contribution. However, total ozone losses are a result of continuous photochemical destruction as ozone is transported from the source region in the tropics to lower altitudes at higher latitudes (Rodríguez *et al.*, 1994), so it is difficult to assess the overall contribution to ozone column trends from instantaneous ozone loss rates. However, 2-D model results indicate that at present abundances of bromine and chlorine in the stratosphere, a 5 pptv increase in inorganic bromine results in a column loss of ozone of 0.5% to 1.0%, with the greater losses occurring at higher latitudes (Isaksen, 1993).

The importance of Cycle I in the lower stratosphere has been ascertained directly from simultaneous *in situ* measurements of the abundances of BrO and ClO and concurrent ozone decreases within the Antarctic ozone hole (Anderson *et al.*, 1990). Analyses using *in situ* BrO and ClO data indicate that Cycle I contributed approximately 25% to ozone losses observed over Ant-

arctica in 1987 (Anderson *et al.*, 1990; Murphy, 1991) and could contribute as much as 40% to total ozone loss over the Arctic in winter (Salawitch *et al.*, 1990, 1993).

On the other hand, because HO<sub>2</sub> measurements have a greater uncertainty (approx. 50%) relative to measurements of BrO (approx. 35%) (Toohey *et al.*, 1990) and ClO (approx. 25%) (Anderson *et al.*, 1990), and because the uncertainty in the rate constant for the BrO + HO<sub>2</sub> reaction at low temperatures is greater than that for the ClO + BrO reaction, the importance of the BrO + HO<sub>2</sub> reaction is less certain. Future simultaneous *in situ* measurements of BrO and HO<sub>2</sub> on the ER-2 aircraft, reductions in BrO and HO<sub>2</sub> measurement uncertainties, and low-temperature kinetics studies will all contribute to a better understanding of the importance of this reaction in the atmosphere, leading to a better assessment of ozone losses due to bromine. However, in the perturbed polar regions where Cycle I dominates, uncertainties in HO<sub>x</sub> kinetics and measurements are of little consequence to estimates of the importance of bromine to ozone losses.

## 10.8 THE OZONE DEPLETION POTENTIAL OF METHYL BROMIDE

### 10.8.1 General Considerations

The concept of Ozone Depletion Potential (ODP) has been extensively discussed in the literature (Wuebbles, 1983; Fisher *et al.*, 1990; WMO, 1990, 1992; Albritton and Watson, 1992; Solomon *et al.*, 1992; Solomon and Albritton, 1992). A single time-independent index has been introduced to quantify the steady-state depletion of ozone by unit mass emission of a given trace species, relative to the same steady-state ozone reduction by unit mass emission of CFC-11. This index, the so-called steady-state ODP, is approximately given by:

$$ODP_{CH_3Br} \equiv \left( \frac{1}{3} \frac{M_{CFC-11}}{M_{CH_3Br}} \frac{\tau_{CH_3Br}}{\tau_{CFC-11}} \beta \right) \left( < \frac{F_{CH_3Br}}{F_{CFC-11}} \alpha > \right)$$

$$ODP_{CH_3Br} \equiv [BLP][BEF] \quad (10-1)$$

where  $M_{CH_3Br}$  and  $M_{CFC-11}$  denote the molecular weight of CH<sub>3</sub>Br and CFC-11,  $F_{CH_3Br}/F_{CFC-11}$  represents the bromine release from CH<sub>3</sub>Br relative to that of chlorine release from CFC-11 in the stratosphere,  $\alpha$  de-

notes the efficiency of the released bromine in catalytic removal of ozone, relative to chlorine;  $\beta$  is the decrease in the mixing ratio of  $\text{CH}_3\text{Br}$  at the tropical tropopause, relative to the mixing ratio at the surface; and  $\langle \rangle$  denotes the spatial and seasonal averaging of the quantity with the appropriate weighting given by the ozone distribution.

The term in the first bracket represents the amount of bromine delivered to the stratosphere by  $\text{CH}_3\text{Br}$  relative to chlorine in CFC-11, per unit mass emission. This is the so-called Bromine Loading Potential (BLP). The second term, the Bromine Efficiency Factor (BEF), denotes the amount of stratospheric ozone removed per unit mass of  $\text{CH}_3\text{Br}$  delivered to the stratosphere, relative to CFC-11. Values for the parameters in Equation 10-1 can be obtained either from global models of the atmosphere (and the ocean) or estimated from observations (Solomon *et al.*, 1992; Solomon and Albritton, 1992). A fuller discussion of the usefulness of the ODP is given in Chapter 13.

The time constants (lifetimes)  $\tau_{\text{CFC-11}}$  and  $\tau_{\text{CH}_3\text{Br}}$  relate the change in (steady-state) atmospheric burden (B) to a change in anthropogenic emission (S). This therefore places limits on the range that can be chosen for the atmospheric lifetimes (see Sections 10.3 and 10.6) and in the case of  $\text{CH}_3\text{Br}$ :

$$\Delta B_{\text{CH}_3\text{Br}}(\text{kT}) = \Delta S_{\text{CH}_3\text{Br}}(\text{kT/yr}) \tau_{\text{CH}_3\text{Br}} \quad (10-2)$$

This time constant (lifetime) can be obtained by considering all removal processes for the species in question, both atmospheric and surface:

$$\frac{1}{\tau_{\text{CH}_3\text{Br}}} = \frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{strat}}} + \frac{1}{\tau_{\text{ocean}}} + \frac{1}{\tau_{\text{other}}} \quad (10-3)$$

where  $\tau_{\text{OH}}$  denotes the time constant for removal by tropospheric OH (2.0 years; see Section 10.4) assuming the rate constants of Mellouki *et al.* (1992), Zhang *et al.* (1992), and Poulet (1993), and scaling to a lifetime of 6.6 years for methyl chloroform removal by OH;  $\tau_{\text{strat}}$  is the time constant for stratospheric removal (35 years; Section 10.4);  $\tau_{\text{ocean}}$  denotes the time constant for ocean removal (about 3.7 years; Butler, 1994; Section 10.5); and  $\tau_{\text{other}}$  denotes time constants for removal by other sink mechanisms, such as reaction with Cl or biodegradation, which are at this point not well established and

are therefore given a value of zero. Adopting the above values for  $\tau_{\text{OH}}$ ,  $\tau_{\text{strat}}$ , and  $\tau_{\text{ocean}}$ , we obtain a value of:

$$\tau_{\text{CH}_3\text{Br}} \approx 1.3 \text{ years} \quad (10-4)$$

with an uncertainty range of 0.8 to 1.7 years.

Adopting the above value of  $\tau_{\text{CH}_3\text{Br}}$  and taking  $\tau_{\text{CFC-11}} = 50$  years (Kaye *et al.*, 1994), a Bromine Loading Potential of 0.013 is calculated from the expression in the first brackets of Equation 10-1. A Bromine Efficiency Factor (BEF) of 48 is calculated by the Atmospheric and Environmental Research, Inc. (AER) 2-D model, adopting heterogeneous chemistry on background aerosols and the kinetic recommendations of DeMore *et al.*, 1992. Using this value (48), the present estimate for the ODP of  $\text{CH}_3\text{Br}$ , taking into account uncertainties in ocean removal, etc., is

$$\text{ODP}_{\text{CH}_3\text{Br}} \approx 0.6$$

### 10.8.2 Steady-State ODP: Uncertainties

The algorithm given by Equation 10-1 provides a useful framework to estimate the uncertainties in the calculated ODP of  $\text{CH}_3\text{Br}$  due to uncertainties in the different input parameters. Uncertainties in the input parameters and their impact on the calculated ODP are listed in Table 10-7. Uncertainties in the Bromine Loading Potentials are directly calculated from Equation 10-1, while the AER 2-D model has been used to calculate the Bromine Efficiency Factor.

The largest uncertainties in ODP are due to the following:

- Uncertainties in the lifetime of  $\text{CH}_3\text{Br}$ . Values of  $\tau_{\text{CH}_3\text{Br}}$  smaller than 1 year would be possible if ocean uptake, removal by reactions with atomic chlorine, and/or surface biodegradation were fast enough. The value of  $\beta$  is unlikely to be much less than 1; recent measurements suggest a value of 0.9 (Blake *et al.*, 1993).
- Uncertainties in the kinetics of  $\text{BrO} + \text{HO}_2$ . Atmospheric measurements of BrO and (upper limits) for HBr (Section 10.7) indicate that the branching of the  $\text{BrO} + \text{HO}_2$  reaction to the HBr channel is probably much less than 2%. Measurements of HBr below 30 km would further constrain this parameter. There are at present no measurements of either the rate or branching of the above reaction at

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**Table 10-7. Principal uncertainties in calculated steady-state ODP for CH<sub>3</sub>Br.**

Parameter	Value-Range	$\tau_{\text{CH}_3\text{Br}}$ (yrs)	BLP	BEF	ODP
$\tau_{\text{OH}}$	2.0 yr ( $\pm 25\%$ ) <sup>a</sup>	1.1 - 1.5	0.011 - 0.015	48	0.52 - 0.76
$\tau_{\text{ocean}}$	3.7 yr ( $\pm 1.3 - 14$ ) <sup>b</sup>	0.78 - 1.7	0.0078 - 0.017	48	0.37 - 0.80
$\tau_{\text{CFC-11}}$	50 yr ( $\pm 10\%$ ) <sup>c</sup>		0.012 - 0.014	48	0.55 - 0.67
$F_{\text{CH}_3\text{Br}}/F_{\text{CFC-11}}$	1.08 ( $\pm 15\%$ ) <sup>d</sup>			41 - 55	0.52 - 0.70
$k_{\text{BrO}+\text{HO}_2}$	6.3 (2.2 - 18) $\times 10^{-11}$ cm <sup>3</sup> s <sup>-1</sup> <sup>e</sup>			32 - 50	0.41 - 0.64
Branching of BrO+HO <sub>2</sub> → HBr+O <sub>3</sub>	0 (< 2%) <sup>f</sup>			30 - 48	0.38 - 0.61

<sup>a</sup> Kaye *et al.*, 1994; Prather, 1993

<sup>b</sup> Butler, 1994 (Section 10.5)

<sup>c</sup> Kaye *et al.*, 1994

<sup>d</sup> Pollock *et al.*, 1992

<sup>e</sup> DeMore *et al.*, 1992, evaluated at 215 K

<sup>f</sup> Section 10.7

**Table 10-8. Calculated time-dependent ODPs.**

Time Horizon (yr)	TD-ODP ( $\tau_{\text{ocean}} = 3.7$ yr)	TD-ODP ( $\tau_{\text{ocean}} = 1.3$ yr)	TD-ODP ( $\tau_{\text{ocean}} = 14$ yr)
5.0	16	12	18
10	5.3	2.7	7.1
15	3.1	1.5	4.2
20	2.2	1.1	3.0
25	1.8	0.9	2.4
30	1.5	0.7	2.1
Infinite (steady state)	0.6	0.3	0.84

stratospheric temperatures. The uncertainties in the rate of BrO + HO<sub>2</sub> due to the lack of temperature information imply uncertainties in the Bromine Efficiency Factor of the order of 50%.

At the same time, there is no single process whose present estimated uncertainty could reduce the ODP of CH<sub>3</sub>Br below 0.3. Smaller values could be possible if two improbable situations occurred simultaneously and several of the parameters were at the extremes of their error limits.

The “semi-empirical” ODPs discussed by Solomon *et al.* (1992) provide a valuable constraint to the model-based results, particularly if we are interested in the ODP for a particular region of the atmosphere. Larger uncertainties are introduced when steady-state ODPs are derived from the semi-empirical approach, since the

necessary observations are usually not available for a global coverage. This is particularly true for CH<sub>3</sub>Br, where (a) coincidental measurements of the BrO, ClO, and HO<sub>2</sub> are sparse, particularly at midlatitudes, and (b) the existing measurements have uncertainties of 25% for ClO, 35% for BrO, and 50% for HO<sub>2</sub> (see Section 10.7).

Overall, the lower limit for the ODP of CH<sub>3</sub>Br is about 0.3 and its most likely value lies between 0.5 and 1.0 (0.6 with BEF = 48).

### 10.8.3 Time-Dependent ODPs

Previous studies (WMO, 1990, 1992; Albritton and Watson, 1992; Solomon and Albritton, 1992) have shown that species with short atmospheric lifetimes have much larger ODPs over short time horizons than over longer time horizons. Table 10-8 updates previous esti-

mates of the time-dependent ODP of CH<sub>3</sub>Br based on the formulation of Solomon and Albritton (1992) with particular respect to changes adopted in the ocean lifetime including a low value (1.3 years) which is outside the limits set by the analysis of ocean sink processes in Section 10.5.1. Uncertainties in the Bromine Efficiency Factor would lead to the same scaling factors for each time horizon as for the steady-state values in Table 10-7. Over the period of any reasonable lifetime for CH<sub>3</sub>Br (*i.e.*, less than and up to 5 years), its ODP is in excess of 10, indicating that a cessation of emissions of CH<sub>3</sub>Br would have a rapid impact on the extent of stratospheric ozone loss.

## 10.9 CONCLUSIONS

This review of the atmospheric science of CH<sub>3</sub>Br has revealed that many uncertainties still exist in both the sources and sinks for this molecule, although its chemistry in the stratosphere and to a large extent in the troposphere is now mostly resolved. The situation with regard to sources and sinks is complicated by the role of the ocean, which acts both as a source and a sink, with the overall balance still in doubt. The research effort on CH<sub>3</sub>Br has been somewhat limited and this is partly responsible for the uncertainties. In spite of this, there is considerable confidence in our best current estimate of 0.6 for the ODP of CH<sub>3</sub>Br. Consideration of the existing uncertainties indicates that it is improbable that this value would be less than 0.3 or larger than 0.8. Individual points are addressed in more detail in the scientific summary for this chapter.

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