A Literature Survey of Atmospheric Methyl Bromide and Stratospheric Ozone

Prepared for

The Methyl Bromide Industry Panel
Chemical Manufacturers Association

by

N.D. Sze and M.K.W. Ko

November 14, 1991

Atmospheric and Environmental Research, Inc.
840 Memorial Drive
Cambridge, MA 02139

Table of Contents

APPENDICES

1. Executive Summary

This report summarizes a review of published information, particularly with regard to observational data for methyl bromide (CH_3Br) and its atmospheric chemistry and budgets (sources and sinks). The measured tropospheric abundance reported by several groups ranges from 10 to 20 pptv (1 pptv = 1 part in 10^{12} by volume) or corresponds to a global burden of 160 to 320 kilotons. With this level of abundance, CH_3Br is currently the dominant form of organic bromine of importance to the stratospheric bromine budget. It remains unclear, however, whether the range in the observed abundances reflects the true temporal and spatial variations or differences in measurement techniques or calibrations. Intercalibration of data between various measurement groups will help to resolve this issue.

One of the pertinent issues concerns the origins of atmospheric CH_3Br. Despite WMO reports (1985; 1989) that CH_3Br is predominantly anthropogenic, the present study reveals considerable controversy on this issue. We note that there is evidence suggesting that ocean may be the major, if not the dominant, source of atmospheric CH_3Br. In order to resolve this important issue, the following are required:

(a) information on the global production/emission of CH_3Br for the past ~10 years;
(b) accurate determination of the global removal rate or the atmospheric lifetime of CH_3Br;
(c) systematic and coordinated measurements of CH_3Br at selected sites in the next few years;
(d) model simulations of time evolution of atmospheric CH_3Br abundance based on our best knowledge of (a) and (b);
(e) comparison of models with observed abundance of CH_3Br.

The atmospheric lifetime is a calculable quantity based on our knowledge of removal mechanisms for CH_3Br. If we assume that tropospheric OH is the principal sink for CH_3Br, we calculate a lifetime of 1.6 years. Because of the uncertainty in both the mean concentration of tropospheric OH and the rate constant for the reaction of OH with CH_3Br, we estimate that the lifetime has an uncertainty range of about a factor of 4. An accurate measurement of the rate constant for the reaction of OH with CH_3Br will help narrow this uncertainty range. Other removal processes appear to be unimportant except possibly for the reaction with atomic chlorine. The relatively short lifetime of CH_3Br (~1.6 year as estimated by models) makes it possible to experimentally determine its lifetime over the next few years.

Accurate determination of atmospheric lifetime is not only important for quantifying the atmospheric budget for CH3Br but is also crucial for calculating the ozone depletion potential (ODP). Scientists, and policy makers, rely on computer modeling to assess the impact of chemicals on stratospheric ozone depletion. The concept of ODP was introduced to characterize the relative potential of a trace gas to deplete stratospheric ozone (Appendix A). Using the AER one-dimensional model, we calculate a value of 0.6 for the ODP of CH_3Br with an uncertainty range of at least a factor of 10. The large uncertainty in ODP is due, in part, to the uncertainty in lifetime and, in part, to the uncertainties in stratospheric bromine chemistry. Our theoretical and experimental knowledge about atmospheric bromine is less well-developed than atmospheric chlorine. Thus, model predictions concerning bromine impact should be viewed with caution. The calculated ODP values depend on the model calculated concentration of BrO. Although model predictions of BrO appear to be consistent with *in situ* measurements (Brune et al., 1988), measurements of HBr (Park et al., 1989) indicate that the concentration of HBr may be 20 times larger than model predictions. Interpretation of the results is not straight-forward. However, when taken at face value, they appear to be in serious conflict with predicted total bromine loading and the BrO/HBr ratio. This apparent discrepancy implies that there may be a missing source for stratospheric bromine, and/or that the chemical scheme in the model is incomplete or that the kinetic data used is in error. Among other possibilities, a revised chemistry scheme that predicts a larger concentration of HBr in harmony with the Park et al. measurements could lead to a downward revision of the ODPs of all brominated species. Current models need to be improved with kinetics data governing certain key reactions and reliable data on emission rates, and their predictions will have to be confirmed by atmospheric observations (e.g., CH_3Br, HBr, BrO).

2. Introduction

On February 21, 1991, Dr. Kurylo of NASA briefed the Methyl Bromide Global Coalition (MBGC) of the potential contribution of CH_3Br to stratospheric ozone loss. He also mentioned that the current view of CH_3Br is that about 50-75% of emissions may be of anthropogenic origin (WMO, 1985; 1989). In response to Dr. Kurylo's briefing, members of the MBGC, CMA and AER staff identified the following issues pertinent to establishing an adequate scientific basis for possible future policy decisions relating to the atmospheric release of CH_3Br:

1. What are the atmospheric budgets/origins of CH_3Br?
2. How good are the observational data for atmospheric CH_3Br, particularly with regard to defining a secular trend?

3. What is the ODP value and the uncertainty range calculated for CH_3Br?
4. How robust is the tropospheric chemistry of CH_3Br and the stratospheric bromine chemistry?

After a series of discussions with members of MBGC, AER was asked to undertake a highly focussed project to provide a partial assessment of the above issues. The project consists of two main tasks:

Task I: Literature review for data on:

a) Laboratory kinetics
b) Field measurements
c) Removal mechanisms

Task II: Modeling

a) Calculation of atmospheric lifetime
b) Calculation of ODP

Regarding Task I(a), AER engaged the services of Aerodyne Research, Inc. (ARI), a firm specializing in laboratory kinetic measurements, to critically review the kinetic data on CH_3Br and selective bromine mechanisms in the stratosphere. The results, to be discussed in section 3.2, are based on a report prepared by ARI which is included as Appendix C of this report.

A report presented to MBGC details the findings of Tasks I and II presented in sections 3 and 4, respectively (see Appendix B for a complete set of viewgraphs). The report also contains four appendices which are intended to describe and clarify certain definitions, approaches, and methodology adopted in this study.

3. Atmospheric Budget of CH_3Br

3.1 Sources of CH_3Br

Although the WMO reports (1985; 1989) stated that 50-75% of atmospheric methyl bromide (CH_3Br) may be of anthropogenic origin, the underlying reasons and evidence leading to this conclusion were not clearly established. In what follows, we review past published work regarding atmospheric sources of CH_3Br.

Wofsy et al. (1975) estimated a source of 76 kiloton yr^{-1} for CH_3Br based on a tropospheric concentration of 10 pptv (1 pptv = 1 part in 10^{12} by volume) and the removal rate as set by the reaction OH + CH_3Br. This source, they noted, exceeds Klingman's (Klingman, 1974) estimate for the total amount of CH_3Br produced industrially in 1974 by about a factor of 4. They contacted Plonka of Dow Chemical, who is of the opinion that only 25% of the industrial bromine is released to the atmosphere, mainly as a by-product of fumigation. Based on this, Wofsy et al. concluded that CH_3Br is most likely of natural origin, with the sea providing 75-95% of atmospheric CH_3Br. A later paper by Singh et al. (1983) who measured CH_3Br in and over the Eastern Pacific Ocean essentially confirms this view. Their measurements indicate that ocean water over the eastern Pacific (40°N to 32°S latitude) is approximately 250% supersaturated with CH_3Br and they estimate an oceanic source strength of 300 kiloton yr^{-1}, almost a factor of 4 larger than Wofsy et al.'s estimates. Note that Singh et al.'s estimate of the source strength is based on a higher tropospheric concentration of CH_3Br of 23 pptv.

Penkett et al. (1985), however, argued that the predominant source of CH_3Br in the atmosphere is anthropogenic rather than natural. They apparently arrived at this conclusion by noting that annual production of CH_3Br in 1972 was estimated to be about 300 kiloton yr^{-1}. And they further assumed, following Wofsy et al.'s estimates, that about 1/4 of the production (75 kilotons) was emitted to the atmosphere. Using the rate for the reaction OH + CH_3Br, an estimated OH concentration of 4×10^5 cm^{-3} and a CH_3Br global abundance of 226 kilotons (or ~14 pptv) inferred from their measurements, Penkett et al. estimated a total emission (i.e., natural and anthropogenic) of 90 kilotons yr^{-1}, which, along with estimates of industrial release, would imply an anthropogenic contribution of about 83 percent. Penkett et al.'s estimate of the 1972 CH_3Br industrial production of 300 kiloton yr-1 was based on information from Wofsy et al (1975) which actually stated that the total (natural and anthropogenic) source is 75 kilotons/year. This issue, which is fundamental to the understanding of the origins and atmospheric budgets of

CH_3Br, and may have important implications for formulating any future control strategies, must be resolved by scientific methods.

We summarize the source estimates by various investigators in Table (1).

3.2 Removal processes

According to present ideas (Wofsy et al., 1975; Yung et al., 1980; Cicerone, 1981), CH_3Br is principally removed by:

$$CH_3Br + OH \rightarrow CH_2Br + H_2O \qquad (1)$$

in the troposphere.

The rate constant for (1) is given by

$$k = 7.6 \times 10^{-13} \exp(-890/T \pm 200/T).$$

This rate is uncertain by a factor of about 2 at a mean tropospheric temperature of 278°K (see Appendix C). A re-measurement of this rate constant is important for a more accurate determination of the atmospheric lifetime of CH_3Br. Using the AER one-dimensional model (see Appendix D), the calculated lifetime for CH_3Br due to (1) is 1.6 years. The same model calculates a lifetime for $CH_3CC\ell_3$ of about 6.5 years, in good agreement with that derived from the atmospheric lifetime experiment (Prinn et al., 1987).

Other known removal processes include stratospheric photolysis,

$$CH_3Br + h\nu \rightarrow CH_3 + Br \qquad (2)$$

The uv-absorption cross-sections appear to be quite well determined. Since photolysis is restricted to the stratosphere where the region consists of about 10% of total air mass, (2) cannot be an important sink for CH_3Br, although it can still affect the calculated ODP value which partly depends on the rate at which bromine atoms are released from stratospheric CH_3Br. We calculate a lifetime of 50 years due to (2).

Methyl bromide also reacts with NO_3,

$$CH_3Br + NO_3 \rightarrow \text{products} \qquad (3)$$

The rate constant for (3) is about 2 - 3 x 10^{-17} cm^3 s^{-1} at 298°K. We calculated a lifetime for CH_3Br due to (3) of about 40 years or longer. Thus, (3) is unlikely to be an important sink for CH_3Br unless our model significantly underestimates the concentration of tropospheric NO_3.

Recently, work by Keene et al. (1990) suggests that atomic chlorine may be released heterogeneously from seasalt (NaCℓ) in the marine boundary layer. Their model predicts concentrations of atomic chlorine approaching that of OH within the marine boundary layer. If we adopt Keene et al's predicted Cℓ concentration, then the reaction of Cℓ with CH_3Br

$$C\ell + CH_3Br \rightarrow HC\ell + CH_2Br \qquad (4)$$

would yield a lifetime of about 1-3 years. The rate constant for (4) has been experimentally studied by Tschuikow-Roux et al. (1988) and is about a factor of 10 faster than that for (1). However, it should be noted that there are considerable uncertainties in modeling tropospheric Cℓ. The proposed mechanism (Keene et al., 1990) of generating large quantities of reactive chlorine from seasalt is quite speculative and substantially more experimental and modeling work is needed to ascertain its role in the removal of CH_3Br and other halomethanes and haloethanes, including the HCFCs, HFCs and CHF_2Br, a proposed substitute for halons (Talukdar et al., 1991).

3.3 Atmospheric measurements and trends

Atmospheric measurements of CH_3Br have been reported by several groups. In table (2), we summarize their measurements according to location, year, and measurement period. Note that most of the measurements of CH_3Br in remote regions indicate concentrations of around 10-15 pptv except for Singh et al. (1983) who reported an average concentration of 23 pptv. It is not clear whether the difference is due to differences in experimental techniques, calibrations or if it reflects real spatial and temporal variations of CH_3Br. Cicerone et al. (1988) reported that there is no clear evidence of a temporal trend although a trend as large as 0.1 ppt/month cannot be ruled out. Salawitch et al. (1988) have reviewed CH_3Br data and argued that CH_3Br has probably increased significantly, perhaps by a factor of 2, in the past ten years. Model simulation of CH_3Br trends with reliable emission data will help resolve this important issue.

4. Stratospheric Bromine Chemistry

4.1 Stratospheric sources of bromine

Once bromo-methanes (e.g., CH_3Br, halons) enter the stratosphere, they may be photo-decomposed to release bromine atoms. Specifically, for CH_3Br, the following

$$CH_3Br + h\nu \rightarrow CH_3 + Br \quad (5)$$

$$CH_3Br + OH \rightarrow CH_2Br + H_2O \quad (6)$$

$$CH_3Br + O(^1D) \rightarrow CH_2Br + OH \quad (7)$$

are expected to lead to ultimate release of Br atoms into the stratosphere. A review of the kinetic data for the above processes are given in Appendix C.

4.2 Partitioning of Bromine Atoms

A schematic diagram for stratospheric bromine chemistry is given in figure 1. Once released by the organic bromine molecule, the bromine atom is transformed into various species indicated in figure 1. The aggregates of the species, Br, BrO, Br_2, $BrC\ell$, $BrNO_3$, HOBr and HBr, are referred to as the total inorganic bromine, or the BrX species. The exact partitioning of BrX into its components depends on altitude, the rate data for the formation and decomposition rate of each species, and the local concentrations of species such as NO_2, O_3, OH and H_2CO which actively participate in stratospheric bromine chemistry. As we will discuss in section 4.3, BrO and Br are the most reactive forms of BrX that directly participate in the catalytic cycles of ozone removal. One key question in determining the ODP of brominated species is what portion of BrX is in the form of BrO in the lower stratosphere. In our model calculations, BrO is predicted to be one of the major forms (about 40%) of BrX at those altitudes.

The existence of BrO in the lower stratosphere (~18-20 km) is confirmed by Brune et al (1988) and Toohey et al (1990) who reported concentrations of about 8 ± 2 pptv. The model calculated concentration of BrO is in rough agreement with the measured values. However, measurement of HBr reported by Park et al (1989) indicates a concentration of 20 ± 6 pptv at 28 km. Our model calculates a value of 1 pptv at the same altitude, about a factor of 20 less than the observation. This large discrepancy between the model result and observation is suggestive of

possible missing elements in our present understanding of the bromine chemistry. It should also be noted that the comparison between models and observations as a means for model validation is not straightforward. More HBr data from different locations and times of year are needed to test models.

4.3 Bromine catalyzed ozone removal

The bromine atoms released from bromo-methanes may participate in a number of catalytic cycles leading to ozone removal. Wofsy et al. (1975) introduce the following cycles involving Br and BrO with odd oxygen (O, O_3)

$$\left.\begin{array}{ll} Br + O_3 \rightarrow BrO + O_2 & (8) \\ BrO + O \rightarrow Br + O_2 & (9) \end{array}\right\} \quad \text{(I)}$$

and

$$\left.\begin{array}{ll} 2\{Br + O_3 \rightarrow BrO + O_2\} & (8) \\ BrO + BrO \rightarrow 2Br + O_2 & (10) \end{array}\right\} \quad \text{(II)}$$

The sequence (I) is equivalent to

$$O + O_3 \rightarrow 2O_2$$

The sequence (II) is equivalent to

$$O_3 + O_3 \rightarrow 3O_2$$

Studies after 1975 suggested that O_3 may also be removed through the coupling of different classes of radicals (e.g., HO_x, $C\ell O_x$, NO_x). Yung et al. (1980) proposed that the following catalytic cycles involving coupling of BrO with reactive chlorine, nitrogen and hydrogen species could also lead to ozone depletion:

$$
\left.\begin{array}{ll}
Br + O_3 \rightarrow BrO + O_2 & (8) \\
C\ell + O_3 \rightarrow C\ell O + O_2 & (11) \\
BrO + C\ell O \rightarrow Br + C\ell + O_2 & (12) \\
\hline
2O_3 \rightarrow 3O_2 &
\end{array}\right\} \quad \text{(III)}
$$

$$
\left.\begin{array}{ll}
Br + O_3 \rightarrow BrO + O_2 & (8) \\
BrO + NO_2 + M \rightarrow BrNO_3 + M & (13) \\
BrNO_3 + h\nu \rightarrow Br + NO_3 & (14a) \\
NO_3 + h\nu \rightarrow NO + O_2 & (15) \\
NO + O_3 \rightarrow NO_2 + O_2 & (16) \\
\hline
2O_3 \rightarrow 3O_2 &
\end{array}\right\} \quad \text{(IV)}
$$

$$
\left.\begin{array}{ll}
Br + O_3 \rightarrow BrO + O_2 & (8) \\
BrO + HO_2 \rightarrow HOBr + O_2 & (17) \\
HOBr + h\nu \rightarrow OH + Br & (18) \\
OH + O_3 \rightarrow HO_2 + O_2 & (19) \\
\hline
2O_3 \rightarrow 3O_2 &
\end{array}\right\} \quad \text{(V)}
$$

4.4 Key uncertainties

Note that cycles (I) through (V), discussed in the previous section, all involve the BrO radical. Since there are no measurements reported for many other bromine species in the lower stratosphere, observational support for stratospheric bromine chemistry is relatively weak, especially compared to that of chlorine. Although model calculations indicate that the impact of bromine on ozone on a per molecule basis is about an order of magnitude larger than that due to chlorine, there is a lack of data to validate these model results.

There are large uncertainties associated with rate data for certain key bromine reactions. For instance, in order for sequence (IV) to be operative as an ozone depletion cycle, $BrNO_3$ must photo-dissociate into Br and NO_3. However, no measurements have been made (De More et al., 1990) regarding the different possible photolysis products. If alternative dissociation paths exist, such as

$$BrNO_3 + h\nu \rightarrow BrO + NO_2 \quad (14b)$$

$$BrNO_3 + h\nu \rightarrow BrNO_2 + O \quad (14c)$$

then sequence IV will become a null cycle (i.e., no impact on ozone removal). There is a need to ascertain the photolysis products from $BrNO_3 + h\nu$. By analogy, the recommended quantum yield for $C\ell NO_3$ photolysis is taken to be 0.9 for the $C\ell + NO_3$ channel and 0.1 for the $O + C\ell NO_2$ channel (Margitan, 1983; Burrow et al., 1988). It should be noted that this value is based on analysis of six independent studies carried out over a ten year period that showed conflicting results.

Other key reactions for which rate constants are uncertain by at least a factor of two include:

$$Br + HO_2 \rightarrow HBr + O_2$$

$$BrO + HO_2 \rightarrow HOBr + O_2$$

$$BrO + OH \rightarrow \text{products}$$

$$BrO + O \rightarrow Br + O_2$$

$$BrO + NO_2 \rightarrow BrONO_2$$

Accurate determination of the kinetic data for the aforementioned processes will help narrow the range of calculated values for ozone depletion potential of various bromo-methanes including CH_3Br.

Recent work on bromine chemistry is mostly directed towards its potential contribution to the observed ozone depletions over the polar regions (McElroy et al., 1986; Rodriguez et al., 1986; Anderson et al., 1989, Ko et al., 1989; Solomon et al., 1990). The current consensus is that, based on observed *in situ* concentrations of BrO and $C\ell O$, up to 25% of the observed stratospheric polar ozone depletion may be attributed to bromine chemistry (Anderson et al., 1990).

Scientists and policy makers rely on computer modeling to assess the impact of chemicals on stratospheric ozone depletion. Unfortunately, our theoretical and experimental knowledge about atmospheric bromine is much less well-developed than atmospheric chlorine. Thus, model

predictions concerning bromide impact should be viewed with caution. Current models need to be improved with kinetics data governing certain key reactions and reliable data on emission rates, and their predictions will have to be confirmed by atmospheric observations (e.g., CH_3Br, HBr, BrO).

5. References

Anderson, J.G., W.H. Brune, S.A. Lloyd, D.W. Toohey, S.P. Snader, W.L. Starr, M. Loewenstein, and J. R. Podolske (1989) Kinetics of O_3 destruction by $C\ell O$ and BrO within the Antarctic vortex: An analysis based on *in situ* ER-2 data. *J. Geophys. Res.*, **94**, 11,480.

Anderson, J.G., W.H. Brune, and D.W. Toohey (1990) Free radicals within the Antarctic vortex: the effect of CFCs. *Science*, **251**, 39.

Berg, W.W., L.E. Heidt, W. Pollock, P.D. Sperry, and R.J. Cicerone (1984) Brominated organic species in the Arctic atmosphere. *Geophys. Res. Lett.*, **11**, 429-432.

Brune, W.H., E.W. Toohey, J.G. Anderson, W.L. Starr, J.F. Vedder, and E.F. Danielson (1988) *In-situ* northern mid-latitude observations of $C\ell O$, O_3 and BrO inthe wintertime lower stratosphere. *Science*, **242**, 558.

Burrows, J.P., G.S. Tyndall, and G.U. Moortgart (1988) *J. Phys. Chem.*, **92**, 4340-4348.

Cicerone, R.J. (1981) Halogens in the atmosphere. *Rev. Geophys. Space Phys.*, **19**, 123-139.

Cicerone, R.J., L.E. Heidt, and W.H. Pollock (1988) Measurements of atmospheric methyl bromide and bromoform. *J. Geophys. Res.*, **93**, 3745-3749.

DeMore, W.B., S.P. Sanders, D.M. Golden, M.J. Molina, R.F. Hampson, M.J. Kurylo, C.J. Howard, and A.R. Ravishankara (1990) Chemical kinetics and photochemical data for use in stratospheric modeling. *JPL Publication 90-1*, Jet Propulsion Laboratory, Pasadena, CA.

Keene, W.C., A.A.P. Pszenny, D.J. Jacob, R.A. Duce, J.N. Galloway, J.J. Schultz-Tokos, H,. Sievering, and J.-F. Boatman (1990) The geochemical cycling of reactive chlorine through the marine troposphere. *Global Biogeochemical Cycles*, **4**, 407-430.

Klingman, C.L. (1974) U.S. Bureau of Mines *Mineral Yearbook*. U.S. Department of the Interior.

Ko, M.K.W., J.M. Rodriguez, N.D. Sze, M.H. Profitt, W.L. Starr, A. Krueger, E. V. Browell, and M.P. McCormick (1989) Implications of AAOE observations for proposed chemical explanations of the seasonal and interannual behavior of Antarctic ozone. *J. Geophys. Res.*, **94**, 16705-16715.

Margitan, J.J. (1983) Chlorine nitrate photochemistry: photolysis products and kinetics of Cl + $ClONO_2 \rightarrow Cl_2 + NO_3$. *J. Phys. Chem.*, **87**, 674-679.

McElroy, M.B., R.J. Salawitch, S.C. Wofsy, and J.A. Logan (1986) Reductions of Antarctic ozone due to synergistic interactions of chlorine and bromine. *Nature*, **321**, 759-761.

Park, J.H., B. Carli, and A. Barbis (1989) Stratospheric HBr mixing ratio obtained from infrared emission spectra. *Geophys. Res. Lett.*, **16**(8), 787-790.

Penkett, S.A., B.M.R. Jones, M.J. Rycroft, and D.A. Simmons (1985 An interhemispheric comparison of the concentrations of bromine compounds in the atmosphere. *Nature*, **318**, 550-553.

Prinn, R., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser, and R. Rosen (1987) Atmospheric trends in methylchloroform and the global average for hydroxyl radical. *Science*, **238**, 945-950.

Rodriguez, J. M., M. K. W. Ko, and N. D. Sze (1986) Chlorine chemistry in the Antarctic stratosphere: Impact of OC*l*O and $C\ell_2O_2$ and implications for observations. *Geophys. Res. Lett.*, **13**, 1292-1295.

Salawitch, R.J., Wofsy, S.C., and M.B. McElroy (1988) Chemistry of OC*l*O in the Antarctic stratosphere: implications for bromine. *Planet. Space Sci.*, **36**, 213-224.

Singh, H.B., L.J. Salas, and R.E. Stiles (1983) Methyl halides in and over the Eastern Pacific. *J. Geophys. Res.*, **88**, 3684-3690.

Solomon, S., R.W. Sanders, and H.L. Miller, Jr. (1990) Visible and near-ultraviolet spectroscopy at McMurdo station, Antarctica, 7, OC*l*O diurnal photochemistry and implications for ozone destruction. *J. Geophys. Res.*, **95**, 13,807.

Talukdar, K., A. Mellouki, T. Gierczak, J.B. Burkholder, S.A. McKeen, and A.R. Ravishankara (1991) Atmospheric lifetime of CHF2Br, a proposed substitute for halons. *Science*, **252**, 693-695.

Toohey, D.W., and J.G. Anderson (1990) *In situ* measurements of BrO in the Arctic stratosphere. *J. Geophys. Res.*, **17**, 513-516.

Tschuikow-Roux, E., F. Faraji, S. Paddison, J. Niedzielski, K. Miyokawa (1988) Kinetics of photochlorination of halogen (F, C*l*, Br) substituted methanes. *J. Phys. Chem.*, **92**, 1488-1495.

WMO (1985) *Atmospheric Ozone 1985*. Global Ozone Research and Monitoring Project -- Report No. 16. World Meteorological Organization, Geneva, Switzerland.

WMO (1989) *Scientific Assessment of Stratospheric Ozone: 1989*. Global Ozone Research and Monitoring Project -- Report No. 20. World Meteorological Organization, Geneva, Switzerland.

Wofsy, S.C., M.B. McElroy, and Y.L. Yung (1975) The chemistry of atmospheric bromide. *Geophys. Res. Lett.*, **2**, 215-218.

Yung, Y.L., J.P. Pinto, R.T. Watson, and S.P. Sander (1980) Atmospheric bromine and ozone perturbations in the lower stratosphere. *J. Atmos. Sci.*, **37**, 339-353.

Table 1. Estimated Sources of Methyl Bromide

Investigators	Total Source strength (kt/yr)	Origin	
		Mostly Natural	Mostly Anthropogenic
Wofsy et al. (1975)	~76	X	
Singh et al. (1983)	~300*	X	
Penkett et al. (1985)	~90		X
WMO/NASA (1985; 1989)	~100		X

*estimate based on oceanic source

Table 2. Tropospheric abundance of CH_3Br

Time period	Location	Remarks	Result
1979-1981 Singh et al	Point arena, 39°N	4-6 samples per month	20 pptv (mean) 10-30 pptv
1980, May Singh et al	Houston St. Louis Denver Riverside	1 week 1 week 1 week 1 week	45-278 pptv 7-125 pptv 23-227 pptv 43-1033 pptv
March 81	Staten Island Pittsburgh Chicago	1 week 1 week 1 week	27-671 pptv 27-62 pptv 21-96 pptv
December, 1981 Singh et al	ship cruise 40°S to 40°N Pacific coast along the America	20 days cruise	19 pptv in South 26 pptv in north up to 50 pptv near 30°N
1982, 1983 Penkett et al	ship cruise 80°N to 80°S	Atlantic UK to Antarctica	10 pptv in south 15 pptv in north
March/April 1983 Berg et al	Arctic	surface to 8 km	11 pptv (mean) 7-24 pptv
1983 Rasmussen et al	Arctic	weekly sampling for 1 year, 30 samples	10 pptv
1985-1987 Cicerone et al	Alaska Mauna Loa Cape Kumukahi Samoa New Zealand	750 samples	11 pptv 10.8 pptv 11.4 pptv 10.2 pptv 9.6 pptv

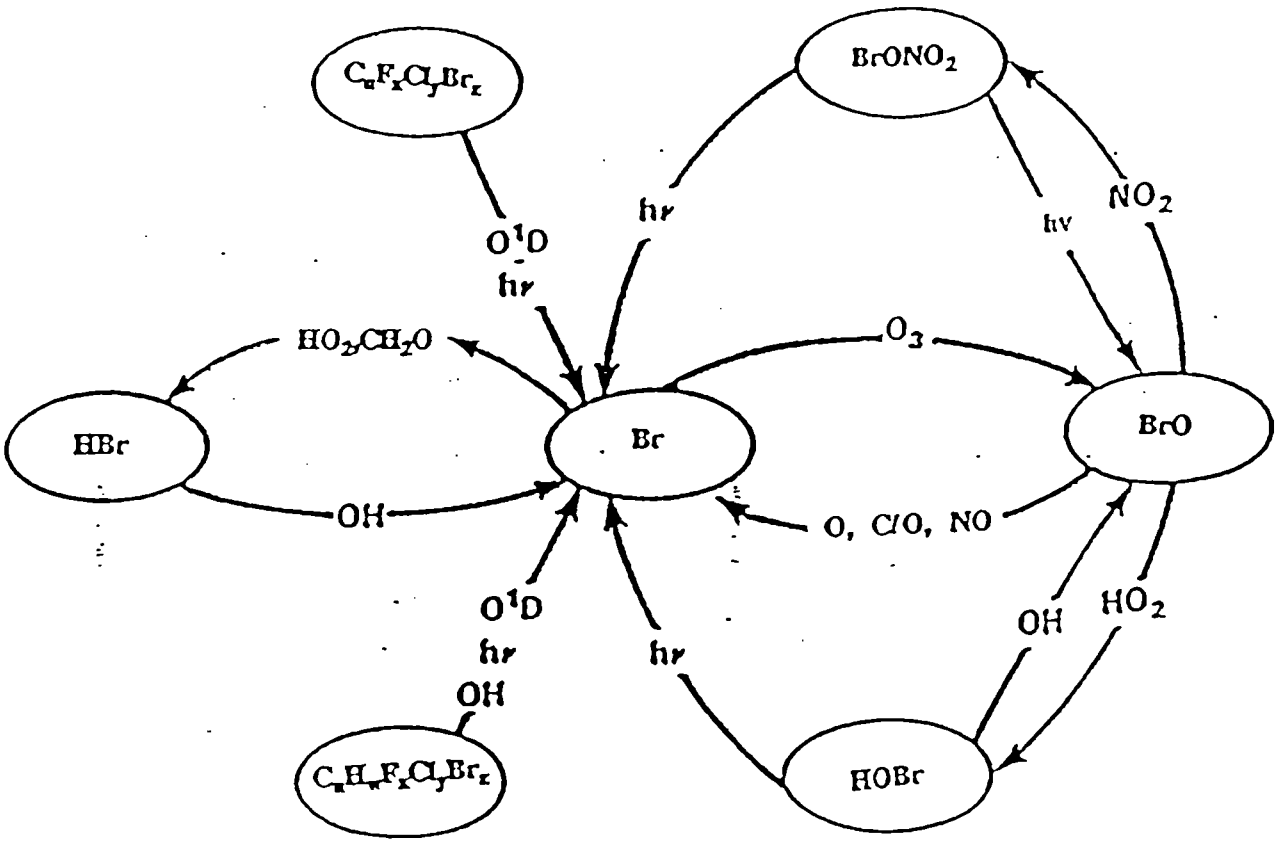


Figure 1. Bromine Cycle

Appendix A

Definitions of atmospheric lifetimes, bromine and chlorine loadings and ozone depletion potential

Atmospheric Lifetime

The atmospheric lifetime of a trace gas provides indications of how rapidly the atmospheric burden will increase if the gas is emitted into the atmosphere; and how fast the gas will be removed from the atmosphere once the emission stopped. The lifetime defined below is the so-called e-folding lifetime. It is the decay time constant that corresponds to the time period in which the atmospheric burden will decrease by 63% if there is no emission.

The atmospheric burden of a gas is given by the equation

$$\frac{dN}{dt} = E - \frac{N}{\tau} \qquad \text{(A1)}$$

where N is the burden, E is the emission rate and τ is the atmospheric lifetime. The parameters are related to certain observables in the following special cases :

(1) If the burden at $t=t_0$ is N_0, and $E = 0$, then, $N(t) = N_0 e^{-t/\tau}$ showing that τ is the e-folding lifetime.

(2) If E is constant in time,and $N(t_0) = 0$, then $N(t) = E\tau(1-e^{t/\tau})$. Note that a steady state is achieved when the emission is balanced by removal resulting in a steady state burden given by

$$N_{ss} = E\tau$$

(3) If values of the burden and emission are available from observation over a sufficient long period of time, τ can be derived from the data using equation (A1).

Alternatively, the atmospheric lifetime of a compound X can be calculated using photochemical models that incorporate the removal mechanisms (e.g., reaction with OH) with measured rate constants and the calculated trace gases (e.g., OH) that react with X. These values can be partially validated by comparison of the model calculated results with corresponding observed quantities.

Bromine and Chlorine Loadings

The impact on ozone from bromine and chlorine containing chemicals, among other factors, is proportional to the concentration of bromine and/or chlorine atoms released by the organic chemicals in the stratosphere. The concentration of stratospheric bromine (chlorine) atoms can be estimated from the concentration of the organic chemical in the troposphere as given by the following equation

$$\text{bromine (chlorine) loading} = f \times n$$

where f is the concentration of the chemical in the troposphere and n is the number of bromine (chlorine) atoms per molecule.

Ozone Depletion Potential

The amount of stratospheric ozone decrease caused by addition of chlorine and bromine containing chemicals depends on the spatial and temporal distributions of the reactive forms of bromine and chlorine as well as the bromine and chlorine loadings. The fraction of reactive forms relative to total loadings is determined by the adopted photochemical scheme with rate data taken from De More et al. (1990). The actual decrease in ozone due to specific emission of a chemical can be calculated using photochemical models. A model may be viewed as a depository of current knowledge and information that provides the basis and capability to simulate the present day atmosphere and to predict future changes.

The ozone depletion potential (ODP) is a measure of the potency of halocarbon specie in removing ozone on a per pound emitted basis relative to CFC-11. The ODP for a chemical Y is calculated using the numerical model as follows. The model is first used to calculate the ozone content in the present day atmosphere. A separate simulation is performed in which the addition of CFC-11 at E kiloton/year is included. The percent change in ozone content between the two simulations is calculated to be A%. The simulation is repeated again with addition of chemical Y at E kiloton/year. The calculated change in ozone relative to the present day atmosphere is B%. Then, ODP for chemical Y is B/A. Note that ODP does not depend on the absolute emission rate. To the extent that ODP depends on bromine (chlorine) loadings, it is also proportional to atmospheric lifetime. Thus, if every factor remains identical, then a shorter lifetime will imply a lower ODP.

References

DeMore, W.B., S.P. Sanders, D.M. Golden, M.J. Molina, R.F. Hampson, M.J. Kurylo, C.J. Howard, and A.R. Ravishankara (1990) Chemical kinetics and photochemical data for use in stratospheric modeling. *JPL Publication 90-1*, Jet Propulsion Laboratory, Pasadena, CA.

Appendix B

Atmospheric Methyl Bromide and Stratospheric Ozone

Presented to

The Methyl Bromide Panel
Chemical Manufacturers Association

Prepared by

N.D. Sze
M.K.W. Ko

Atmospheric and Environmental Research, Inc.
840 Memorial Drive
Cambridge, Massachusetts 02139

Outline of Presentation

- Summary of Issues
- Budget and Sources of Atmospheric Methyl Bromine

  Atmospheric Lifetime
  Sources of Methyl Bromine

- Review of Atmospheric Measurements

  Burden
  Trend

- Potential Impact on Stratospheric Ozone and Ozone Depletion Potential

  Stratospheric Bromine Chemistry
  Model Determined Values of ODP

- Sources of Uncertainties on Ozone Depletion Potential

  Atmospheric lifetime of methyl bromine and bromine loading
  Bromine-ozone relation

- Recommendations

Summary of Issues

1. Atmospheric budgets/origins of CH_3Br

2. Preliminary model calculation of ozone depletion potential (ODP)

3. Sources of major uncertainties

4. Recommendations

Issue #1

Atmospheric Budgets/Origins of CH_3Br

		Uncertainty Range
Concentration (ppt)	~12	10 - 20
Burden (kiloton)	~189	159-315
Lifetime (yr)	~1.6	.7 - 2.5
Annual removal rate (kiloton/yr-1)	~118	63 - 450

Issue #2

Preliminary Model Calculation of Ozone Depletion Potential (ODP)

$$ODP = 0.6 \quad \left\{ \begin{array}{c} \text{Uncertainty range} \\ .15 - .8^{(1)} \\ .26 - .9^{(2)} \\ .07 - 1.2^{(3)} \end{array} \right.$$

(1) due only to uncertainty in stratospheric bromine chemistry

(2) due only to uncertainty in atmospheric lifetime

(3) combined uncertainty

Removal Processes for CH_3Br

$$\text{Total Lifetime } \frac{1}{\tau_T} = \sum_{i=1}^{n} \frac{1}{\tau_i}$$

(1) $CH_3Br + OH \rightarrow CH_2Br + H_2O$

$k = 7.6 \times 10^{-13} \exp(-\frac{890}{T})$ $cm^3\ s^{-1}$

$\tau_{OH} = 1.6$ years

(2) $CH_3Br + Hv \rightarrow CH_3 + Br$

$\lambda = 210 - 290$ nm

$\tau_{hv} \approx 50$ years

(3) $CH_3Br + NO_3 \rightarrow CH_2Br + HNO_3$

$k \approx 2\text{-}3 \times 10^{-17}$ $cm^3\ s^{-1}$

$\tau_{NO_3} > 40$ years

(4) Hydrolysis (?)

Sources of Methyl Bromide

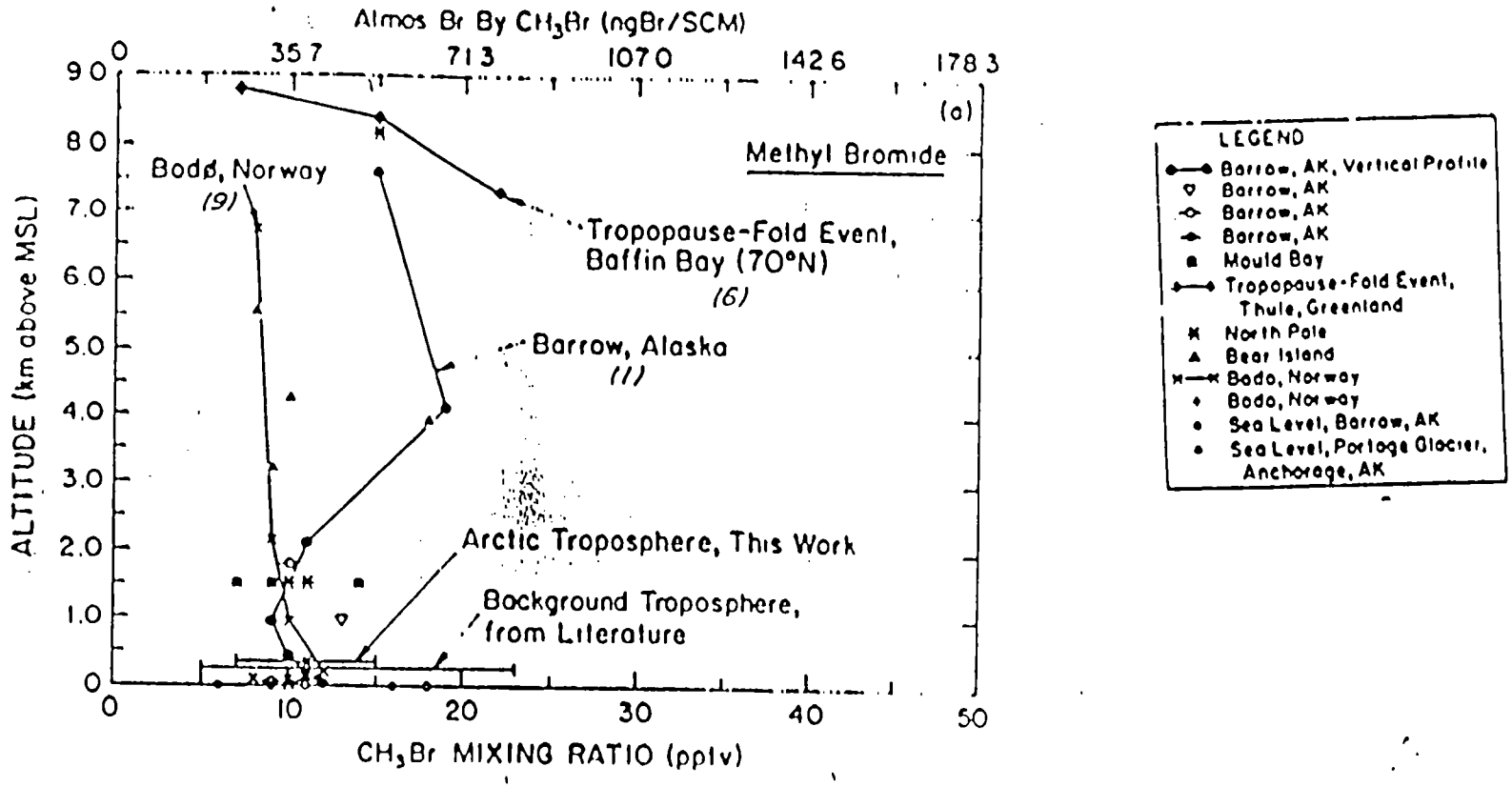
Investigators	Source strength (kt/yr)	Origin	
		Natural	Anthropogenic
Wofsy et al. (1975)	~76	X	
Singh et al. (1983)	~300*	X	
Penkett et al. (1985)	~90		X
WMO/NASA (1985; 1989)	~100		X

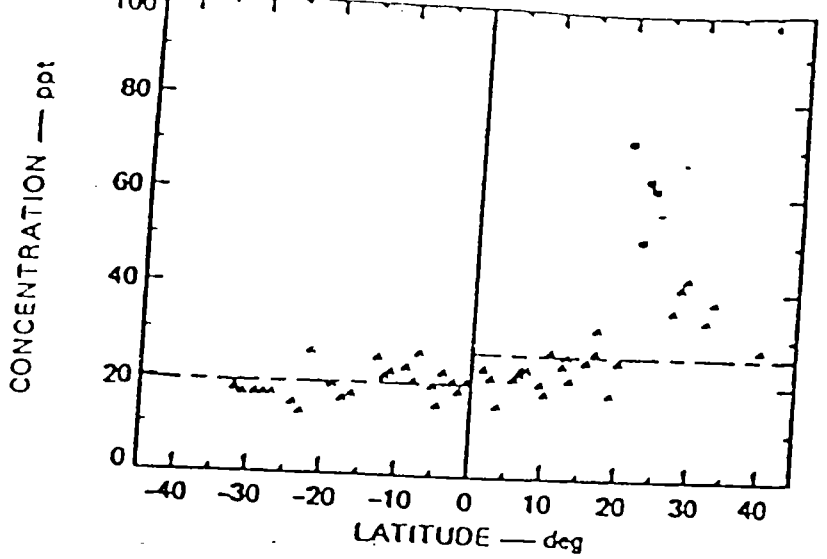
*estimate based on oceanic source

Atmospheric Measurements

Tropospheric abundance of CH_3Br

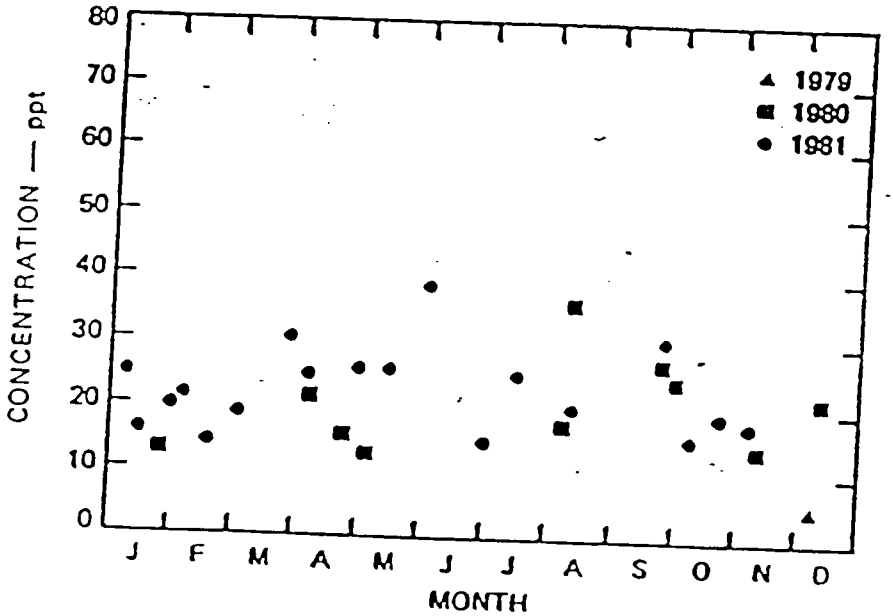
Time period	Location	Remarks	Result
1979-1981 Singh et al	Point arena, 39°N	4-6 samples per month	20 pptv (mean) 10-30 pptv
1980, May Singh et al	Houston St. Louis Denver Riverside	1 week 1 week 1 week 1 week	45-278 pptv 7-125 pptv 23-227 pptv 43-1033 pptv
March 81	Staten Island Pittsburg Chicago	1 week 1 week 1 week	27-671 pptv 27-62 pptv 21-96 pptv
December, 1981 Singh et al	ship cruise 40°S to 40°N Pacific coast along the America	20 days cruise	19 pptv in South 26 pptv in north up to 50 pptv near 30°N
1982, 1983 Penkett et al	ship cruise 80°N to 80°S	Atlantic UK to Antarctica	10 pptv in south 15 pptv in north
March/April 1983 Berg et al	Arctic	surface to 8 km	11 pptv (mean) 7-24 pptv
1983 Rasmussen et al	Arctic	weekly sampling for 1 year, 30 samples	10 pptv
1985-1987 Cicerone et al	Alaska Mauna Loa Cape Kumukahi Samoa New Zealand	750 samples	11 pptv 10.8 pptv 11.4 pptv 10.2 pptv 9.6 pptv


Almos Br By CH_3Br (ngBr/SCM)
0
35.7
71.3
107.0
142.6
178.3
(a)
Methyl Bromide
Bodø, Norway
(9)
Tropopause-Fold Event,
Baffin Bay (70°N)
(6)
Barrow, Alaska
(1)
Arctic Troposphere, This Work
Background Troposphere,
from Literature
ALTITUDE (km above MSL)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0
10
20
30
40
50
CH_3Br MIXING RATIO (pptv)
LEGEND
Barrow, AK, Vertical Profile
Barrow, AK
Barrow, AK
Barrow, AK
Mould Bay
Tropopause-Fold Event,
Thule, Greenland
North Pole
Bear Island
Bodo, Norway
Bodo, Norway
Sea Level, Barrow, AK
Sea Level, Portage Glacier,
Anchorage, AK



(b) METHYL BROMIDE

Fig. 3. Latitudinal distribution of methyl halides. Dashed lines indicate weighted hemispheric averages. Darkened squares are excluded from these averages for statistical reasons. Positive latitudes are °N; negative latitudes are °S.



(b) METHYL BROMIDE

Fig. 4. Methyl halide concentrations at Point Arena (39°N). Each data point is an average of 4 to 6 samples.

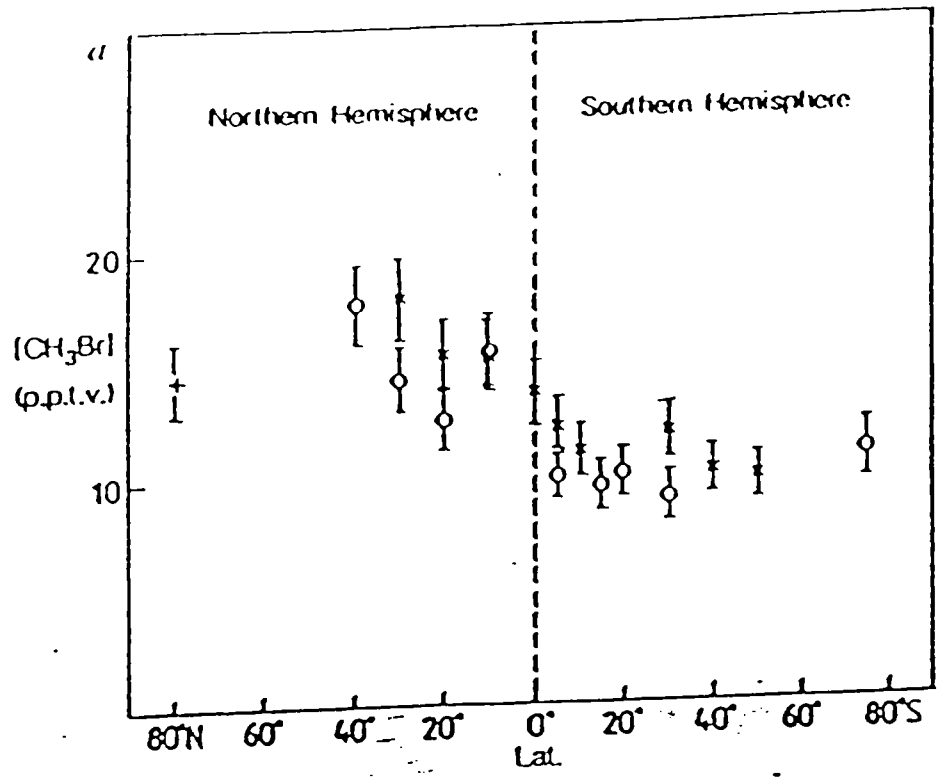


Fig. 1 Longitudinal transepts of the concentrations of four bromine compounds: *a*, CH_3Br; *b*, CH_2Br_2, *c*, $CHBr_3$; *d*, CF_3Br. ○, 1982 voyage via Cape Town; ×, 1983 voyage via Rio; +, values collected on other experiments.

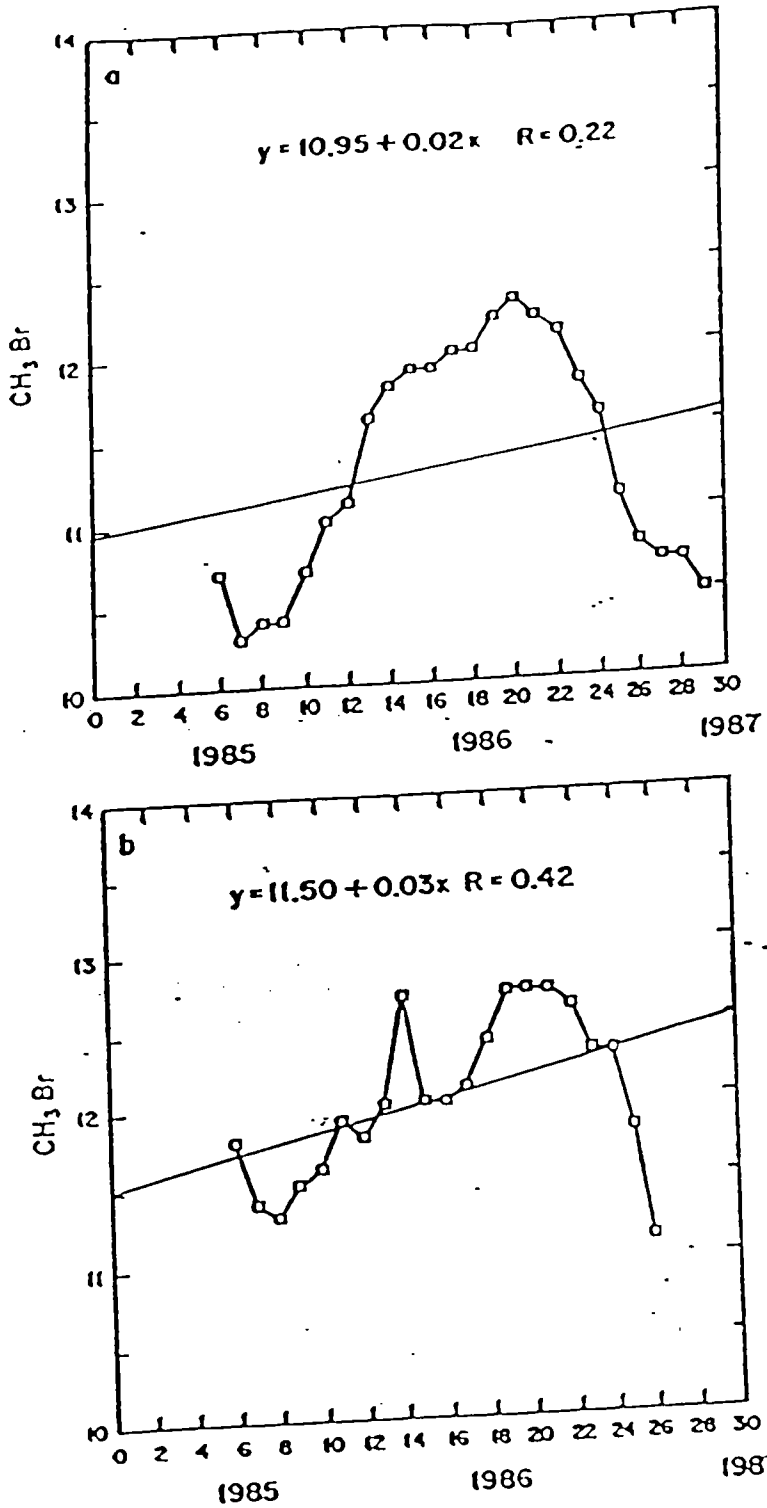
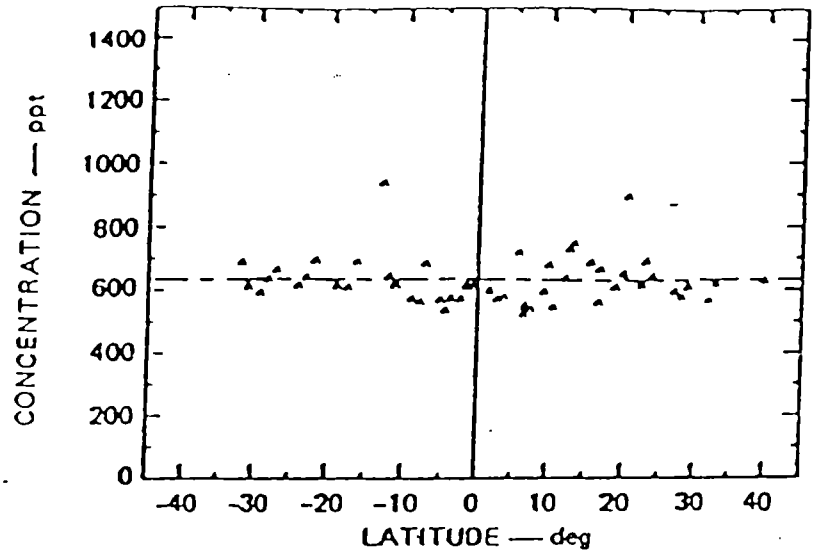


Fig. 1. Twelve-month running averages of CH_3Br mole fractions (ppt = 10^{-12}) measured at (a) Point Barrow, Alaska, and (b) Cape Kumukahi, Hawaii, during a 34-month period that began in January 1986. Equations for regression-line fits to the data are displayed in each panel; slopes are measured in ppt per month. R values are correlation coefficients.

Trend

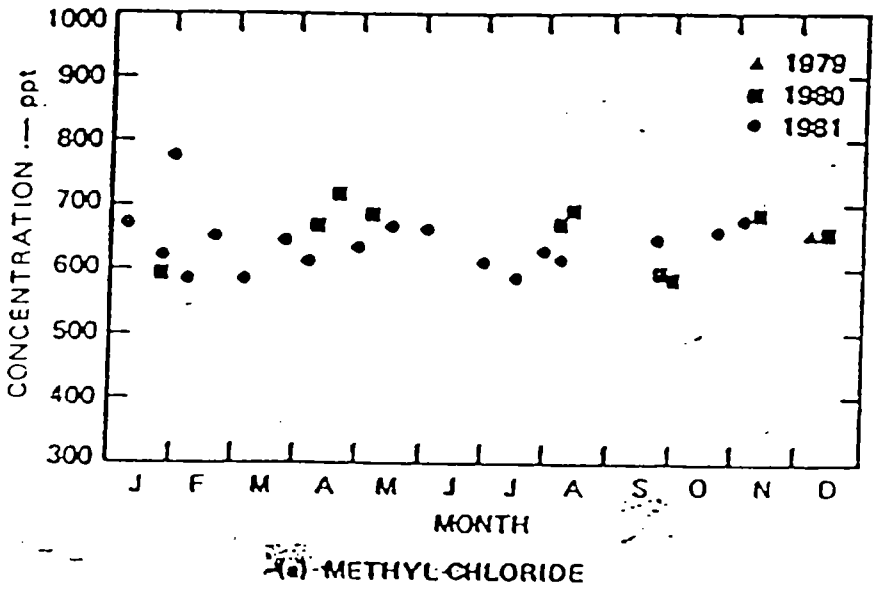
The only data that discusses trend is from the monitoring at five sites. Cicerone et al. reported that there is no clear indication of a temporal trend although a trend as large as 0.1 pptv/month cannot be ruled out.

From the budget point of view, current concentration of 12 pptv implies that a source of 118 kilotons/year is needed to maintain concentration. An additional 34 kilotons/year will cause a 1 pptv/year increase in concentration.



(a) METHYL CHLORIDE

Fig. 3. Latitudinal distribution of methyl halides. Dashed lines indicate weighted hemispheric averages. Darkened squares are excluded from these averages for statistical reasons. Positive latitudes are °N; negative latitudes are °S.



(a) METHYL CHLORIDE

Fig. 4. Methyl halide concentrations at Point Arena (39°N). Each data point is an average of 4 to 6 samples.

TABLE 2. Independent Existence of High Methyl Chloride and Methyl Iodide Concentrations in Seawater

Latitude*	Surface Seawater Concentration, ng/l		
	CH_3Cl	CH_3Br	CH_3I
22.68	41.8	3.7	0.9
20.19	18.1	1.5	1.0
−8.68	10.6	1.5	3.2
−8.99	22.5	2.9	2.4
−9.50	9.8	1.2	6.8
−11.70	8.7	1.9	4.2
−12.83	10.6	1.1	3.7
−16.93	26.7		3.5

*Positive latitude is °N; negative latitude is °S.

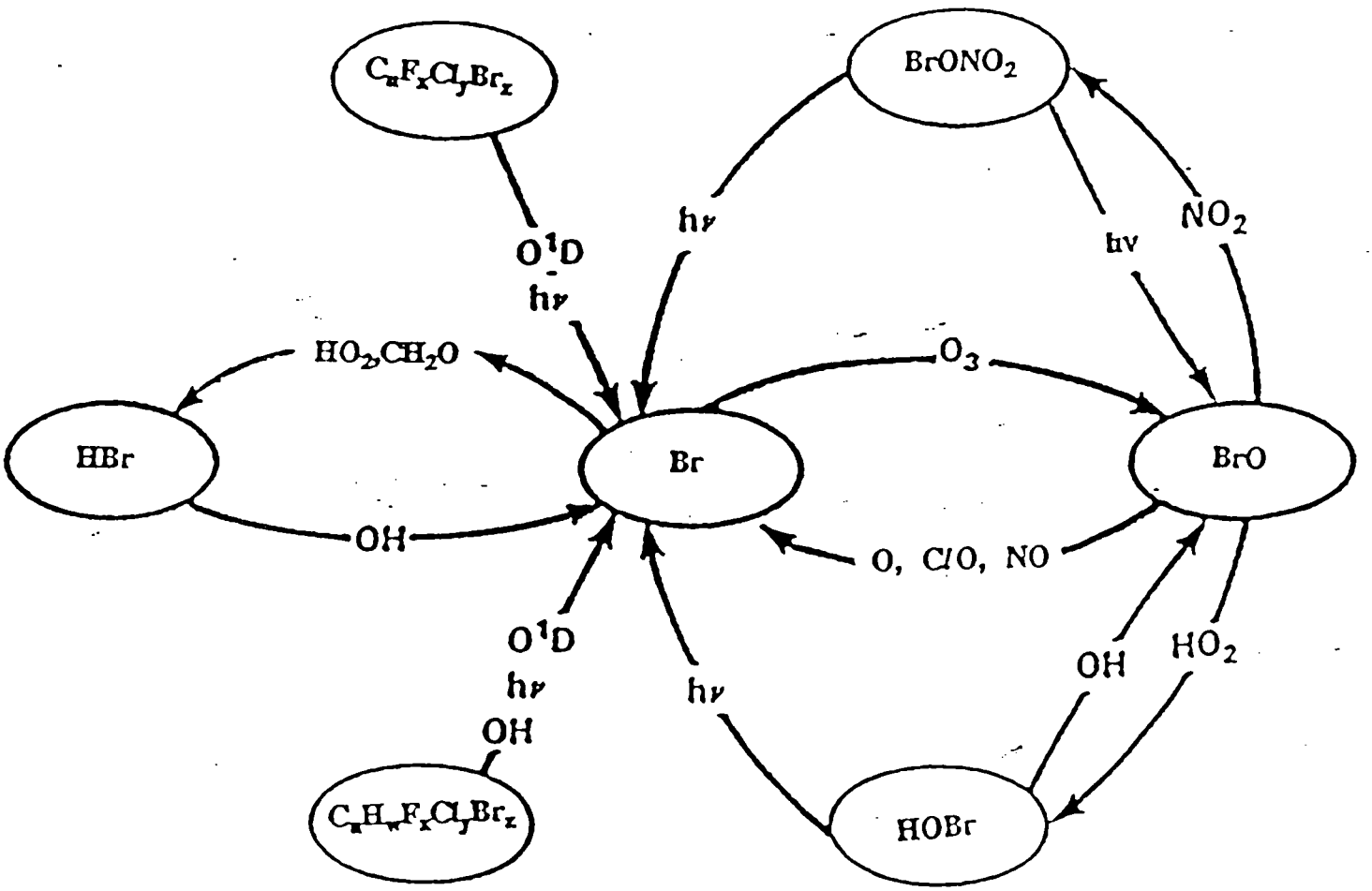
TABLE 3. Estimated Oceanic Methyl Halide Source Strength

Chemical Name	Average Concentration		Ocean Supersaturation, %	Extrapolated Ocean to Air Flux, 10^{-7} g cm^{-2} yr^{-1}	Global Oceanic Source, Tg/yr	Estimated Atmospheric Residence Time From Oceanic Source Alone, years*
	Seawater ng/l	Air, ppt				
Methyl chloride	11.5	633	275	13.3	4.9	1.2
Methyl bromide	1.2	23	250	0.9	0.3	1.2
Methyl iodide	1.6	2	336	1.4	0.5	0.09
	1.0		210	0.9	0.3	0.15

*Assuming the air and seawater concentration to be representative of troposphere and oceans, respectively. See text for discussion.

Stratospheric Bromine Chemistry

BROMINE CYCLE



Stratospheric Sources of Bromine

$$C_wH_xCl_yBr_z + h\nu \rightarrow C_wH_xCl_yBr_{z-1} + Br$$

$$C_wH_xCl_yBr_z + OH \rightarrow C_wH_{x-1}Cl_yBr_{z-1} + H_2O$$

$$C_wH_xCl_yBr_z + O(^1D) \rightarrow \text{Products}$$

Bromine Catalyzed O_3 Depletion

$$\begin{aligned} Br + O_3 &\rightarrow BrO + O_2 \\ Cl + O_3 &\rightarrow ClO + O_2 \\ BrO + ClO &\rightarrow Br + Cl + O_2 \\ \hline 2O_3 &\rightarrow 3O_2 \end{aligned} \qquad (1)$$

$$\begin{aligned} Br + O_3 &\rightarrow BrO + O_2 \\ BrO + BrO &\rightarrow 2Br + O_2 \\ \hline 2O_3 &\rightarrow 3O_2 \end{aligned} \qquad (2)$$

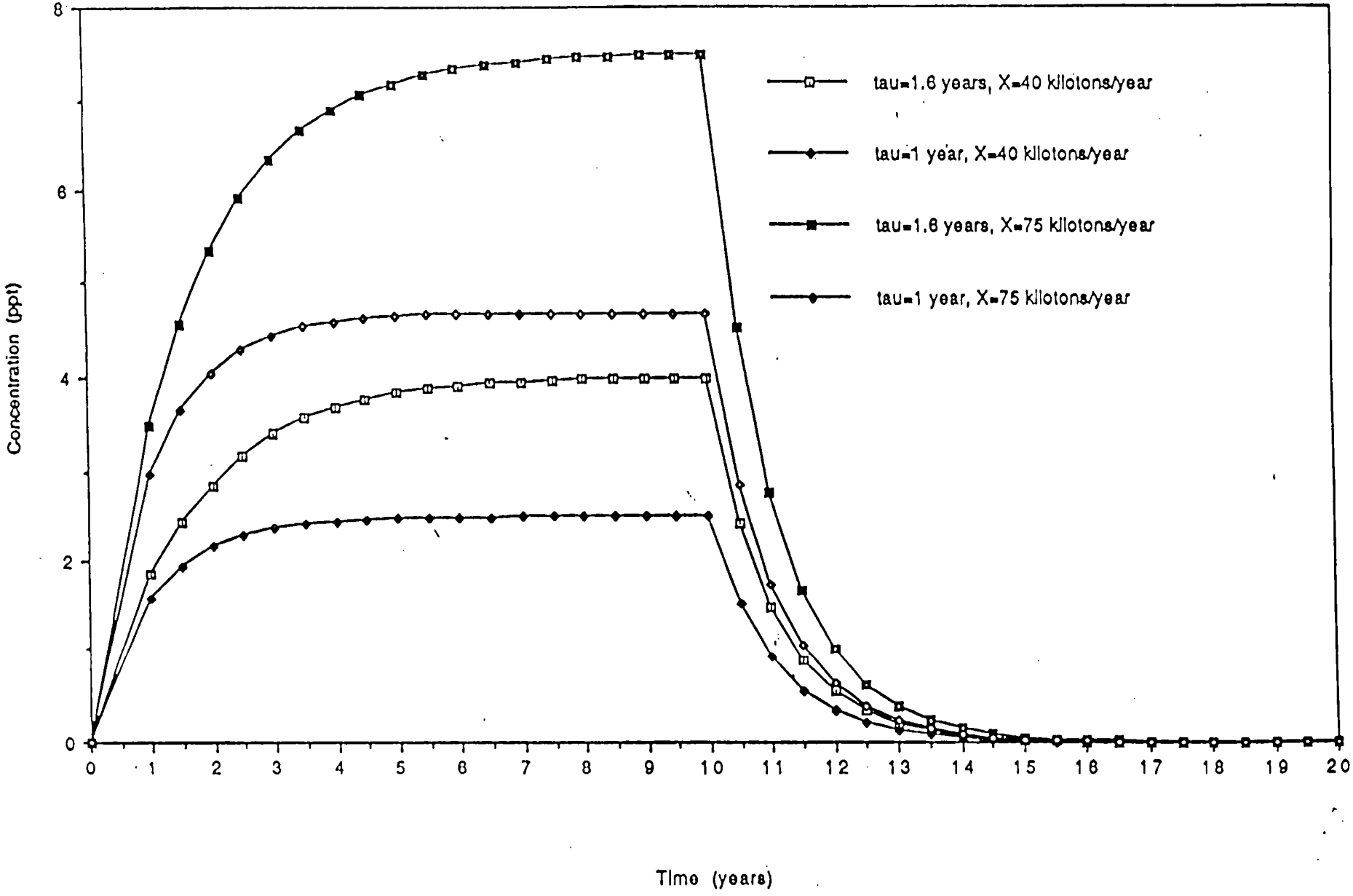
$$\begin{aligned} Br + O_3 &\rightarrow BrO + O_2 \\ BrO + O &\rightarrow Br + O_2 \\ \hline O + O_3 &\rightarrow 2O_2 \end{aligned} \qquad (3)$$

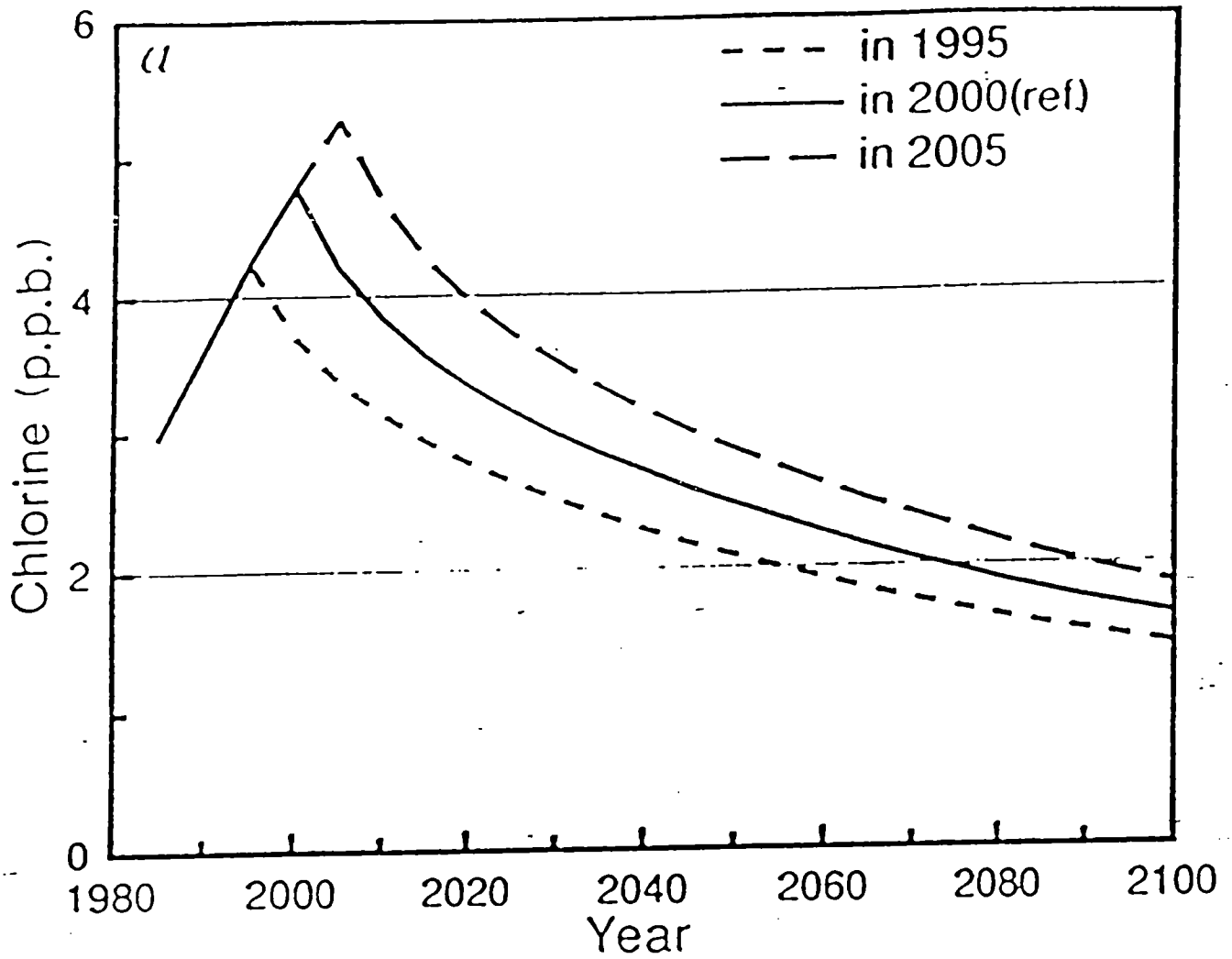
$$\begin{aligned} Br + O_3 &\rightarrow BrO + O_2 \\ NO + O_3 &\rightarrow NO_2 + O_2 \\ BrO + NO_2 &\xrightarrow{M} BrONO_2 \\ BrONO_2 + h\nu &\rightarrow Br + NO_3 \\ NO_3 + h\nu &\rightarrow NO + O_2 \\ \hline 2O_3 &\rightarrow 3O_2 \end{aligned} \qquad (4)$$

$$\begin{aligned} Br + O_3 &\rightarrow BrO + O_2 \\ BrO + HO_2 &\rightarrow BrOH + O_2 \\ BrOH + h\nu &\rightarrow Br + OH \\ OH + O_3 &\rightarrow HO_2 + O_2 \\ \hline 2O_3 &\rightarrow 3O_2 \end{aligned} \qquad (5)$$

Time Dependent Calculations and Trends

Effect of Lifetime (Tau) and Emission Rate on Methyl Bromide Burden.
Emission Rate is X For the First 10 Years and 0 After.




(1
in 1995
in 2000(ref)
in 2005
Chlorine (p.p.b.)
6
4
2
0
1980
2000
2020
2040
2060
2080
2100
Year

Recommendations

Reduce the uncertainties in the Ozone Depletion Potential by validating the atmospheric lifetime of methyl bromine and the bromine-ozone relation

Issue #1: Atmospheric budget and origin:

Laboratory kinetic measurements:

Kinetics of methyl bromine to determine lifetime

Field measurements:

Burden, trend, and intercalibration

Modeling:

Tropospheric chemistry

tropospheric OH

tropospheric chlorine chemistry

Simulation of burden and trend from emission data using 1-D and 2-D models

Issue #2: Bromine-ozone relation

Laboratory kinetic measurements:

Bromine chemistry

Modeling:

Heterogeneous chemistry

Appendix C

EVALUATION OF THE ATMOSPHERIC CHEMICAL KINETICS OF METHYLBROMIDE

Prepared by

C.E. Kolb
Center for Chemical and Environmental Physics
Aerodyne Research, Inc.
45 Manning Road
Billerica, MA 01821

Prepared for

Atmospheric and Environmental Research, Inc.
Cambridge, MA 02139

and

The Chemical Manufacturers Association
Washington, DC 20037

May 1991

EVALUATION OF THE ATMOSPHERIC CHEMICAL KINETICS OF METHYL BROMIDE

ABSTRACT

Reaction rate constants and photodissociation cross sections of potential importance in determining the atmospheric lifetime of methyl bromide (CH_3Br) have been reviewed and evaluated. Reactions with OH, Cl, $O(^1D)$, $O(^3P)$, HO_2 and NO_3 have been considered along with ultraviolet photodissociation.

INTRODUCTION

Methyl bromide is a trace constituent of the Earth's atmosphere with both natural and anthropogenic sources. The major interest in atmospheric methyl bromide has focused on its role as a source for stratospheric Br and BrO, which participate in the halogen catalyzed destruction of the stratospheric ozone layer. Initial modeling studies of this effect by Wofsy et al. (1975) and Yung et al. (1980) restricted atmospheric destruction of CH_3Br to reaction with hydroxyl radicals (OH) and photodissociation. Quite recent models designed specifically to calculate the atmospheric lifetimes of halocarbons still restrict CH_3Br degradation to these two processes (Prather and Spivakovsky, 1990; Prather, 1991). National Institute of Standards and Technology (NIST) staff have concluded that these two processes will also dominate the atmospheric degradation of hydrogen containing bromocarbon compounds including CH_2Br_2 (Gann et al., 1990).

Grogjean (1991) has just published an analysis of the tropospheric chemistry of methyl bromide. He concludes that the reaction with OH is slow and reactions with O_3 and NO_3 are negligible. He suggests that the loss for the lower tropospheric is upward diffusion or deposition. He also concludes that CH_3Br is not formed within the atmosphere. Methyl bromide may also play a minor role in the springtime destruction of tropospheric ozone in the arctic, although bromoform ($CHBr_3$) rather than CH_3Br is believed to be the major driver for that recently discovered phenomena (Barrier et al., 1988).

This short report will document and evaluate chemical kinetic and photodissociation processes which may influence the atmospheric lifetime of CH_3Br. It also contains a brief analysis of the photochemistry and reaction kinetics of active stratospheric bromine species such as Br, BrO, $BrONO_2$, HOBr and HBr.

PHOTODISSOCIATION OF CH_3Br

The weakest bond in methyl bromide is the C-Br bond, with a dissociation energy at 298°K of 292 ± 8 kJ/mole or 69.8 ± 2 kcal/mole (Tschuikow-Roux and Paddison, 1987). This corresponds to a possible photodissociation threshold of only 410 nm. However, measurable absorption does not begin until about 290 nm in the near ultraviolet, ensuring that CH_3Br photodissociation does not occur below the stratosphere. Photoabsorption cross sections for CH_3Br have been measured by Robbins (1976), Molina et al. (1982), Uthman et al. (1978) and Gillotay and Simon (1988). The agreement between these studies is very good.

Gillotay and Simon extended the previous room temperature measurements down to 209 K. A plot of their room temperature data compared to Robbins data is shown in Figure 1. A tabular comparison of 295 K data from three of the measurements along with selected lower temperature data from Gillotay and Simon (1988) is presented in Table 1. The data of Molina et al. do extend to 290 nm with a measured cross section of 3×10^{-24} cm^2 at 298 K for that wavelength.

It is probably a safe assumption that the photoabsorption cross sections shown in Figure 1 and Table 1 lead to a breaking of the C-Br bond with unit quantum yield. However, the C-H bonds in CH_3Br have a dissociation energy at 298 K of 425 ± 4 kJ/mole indicating that photoabsorption at wavelengths of 282 nm or shorter could also break the C-H bond. Which bond is broken may be immaterial under stratospheric photochemical conditions.

REACTION KINETICS OF CH_3Br

Methyl bromide is a stable, saturated compound and can be expected to react only with free radical or electronically excited species. Current

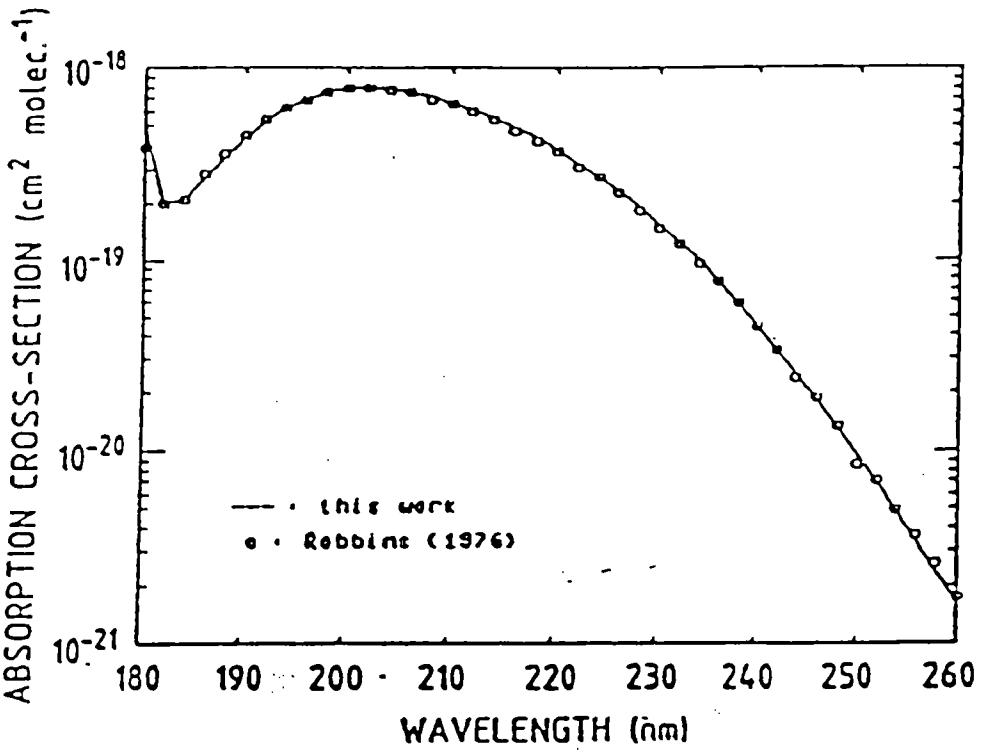


Figure 1. CH_3Br absorption cross-section of with respect to wavelength between 180 and at 260 nm, at 295 K from Gillotay and Simon (1988).

TABLE 1 - CH_3Br absorption cross-section: experimental values at 295 K, 227 K and from Gillotay and Simon (1988) compared with the values of Robbins (1976) and of Molina et al. (1982)

$\sigma(\lambda)$ 10^{21} (cm^2 $molec.^{-1}$)

	This work				Robbins (1976)	Molina et al. (1982)
λ (nm)	295K	255K	227K	209K	295K	295K
180	500	500	500	500	391	
182	198	198	198	198	197	
184	208	208	208	208	211	
186	271	271	271	271	284	
188	346	346	346	346	358	
190	439	439	439	439	447	441
192	529	529	529	529	544	
194	620	620	620	620	626	
196	691	691	691	691	692	
198	760	760	760	760	768	
200	791	791	791	791	796	785
202	797	797	797	797	797	
204	793	793	793	793	778	
206	767	767	767	767	757	
208	727	727	727	727	695	
210	666	666	666	666	657	649
212	614	613	613	613	597	
214	559	558	558	556	547	
216	493	495	494	490	476	
218	442	436	434	433	420	
220	377	374	369	366	375	360
222	324	321	315	312	310	
224	276	275	261	259	270	
226	230	228	213	216	223	
228	188	188	181	177	182	
230	154	151	146	144	146	145
232	124	121	118	114	121	
234	98.7	95.2	90.8	88.6	96.1	
236	76.5	73.4	69.9	65.8	76.4	
238	59.5	55.2	51.6	49.7	58.7	
240	44.7	41.7	39.0	37.9	44.2	41.1
242	33.5	30.2	28.9	27.6	33.0	
244	25.0	22.5	20.7	19.4	23.8	
246	18.2	16.2	14.7	14.2	18.7	
248	13.1	11.3	10.4	9.80	13.4	
250	9.57	8.13	7.31	6.75	8.48	9.49
252	6.86	5.68	4.99	4.47	7.04	
254	4.87	3.88	3.43	3.15	4.95	
256	3.36	2.72	2.32	2.02	3.58	
258	2.35	1.90	1.49	1.29	2.60	
260	1.64	1.37	1.08	0.88	1.72	1.63

models of the troposphere and stratosphere have identified OH, HO_2, NO_3, Cl, O and $O(^1D)$ as the primary reactive radicals which drive atmospheric oxidation. The available reaction rate data for these species with CH_3Br will be evaluated below.

In evaluating the reaction kinetics of CH_3Br I have accessed several data bases and evaluated data compilations, including the NIST Chemical Gas Kinetic Data Base (Release 2) (NIST, 1990), NASA's stratospheric chemical kinetics and photochemical data evaluation (DeMore et al., 1990), IUPAC's atmospheric chemistry kinetic and photochemistry data evaluation (Atkinson et al., 1989), a recent review of OH/organic compound kinetics (Atkinson, 1989), and reviews/evaluations of HO_2 kinetics (Lloyd, 1974; Kaufman and Sherwell, 1983) and O atom kinetics (Herron and Huie, 1973; Herron, 1988).

OH Reaction

The reaction of CH_3Br with OH is presumed to proceed by hydrogen atom abstraction:

$$OH + CH_3Br \rightarrow CH_2Br + H_2O \ . \qquad (1)$$

The reaction has been studied experimentally by Howard and Evenson (1976) at 296 K and Davis et al. (1976) between 245-375 K. These studies agree very well at room temperature. The IUPAC evaluated rate constant (Atkinson et al., 1989) of:

$$k = 7.6 \times 10^{-13} \exp(-890 \pm 200/T) \ cm^3/s \qquad (2)$$

was also adopted in Atkinson's OH/organics review (Atkinson, 1989). NASA's stratospheric evaluation of the same data (DeMore et al., 1990) yielded a slightly different rate constant representation of:

$$k = 6.8 \times 10^{-13} \exp(-850 \pm 200/T) \ cm^3/s \ . \qquad (3)$$

Cohen and Benson (1987) have published a theoretical evaluation of the OH/CH_3Br reaction which is in reasonable accord with the data.

Either the IUPAC or NASA evaluated rate can be used in current models since they are essentially equivalent, with Equation 2 yielding 2.81×10^{-14} and Equation 3 yielding 2.92×10^{-14} cm^3/s evaluated for the mean tropospheric temperature of 270 K.

The NASA evaluation gives an uncertainty factor in the room temperature (298 K) rate of x/÷ 1.25. The temperature dependence uncertainty (E/R ± Δ E/R) is stated as (-850 ± 200). At 270 K this is an uncertainty range of 4.4 just due to exponential factor uncertainty.

The IUPAC evaluation gives a room temperature uncertainty range of $3.8 \times 10^{-14} \pm 0.1$ leading to an uncertainty range of 4.7×10^{-14} to 3.0×10^{-14}. They also estimate the (E/R ± Δ E/R) as (-890 ± 200). At 270 K this is also an uncertainty range of 4.4.

Given the above, it is clear that an uncertainty in the 270 K rate of a range of factor of 5 can be justified. (E g. approximately an uncertainty factor of x/÷ 2.2.)

It should be noted, however, that the reaction with OH could be even slower than indicated by the two experimental measurements. Recent experience with the CH_4 + OH reaction rate (Vaghjiani and Ravishankara, 1991) has shown that slow, low temperature rates can easily be biased by sample impurities. The CH_3Br + OH rate constant should be remeasured with updated techniques over the 300-240°K range relevant to the troposphere and stratosphere.

Cl Reaction

The reaction of CH_3Br with ground state atomic chlorine:

$$Cl + CH_3Br \rightarrow CH_2Br + HCl \qquad (4)$$

has been experimentally studied by Tschuikow-Roux et al. (1988) over the temperature range of 273 to 368 K. The rate constant determined was:

$$k = (3.16 \pm 0.63) \times 10^{-11} \exp(-1205 \pm 69/T)\ cm^3/s\ . \qquad (5)$$

This is the only measurement for this reaction I could locate, so comparative data evaluation is impossible. This group measured comparable rate constants for several other halocarbon compounds. The rate expression is reasonable given the nature and thermochemistry of the reaction.

O Reaction

The reaction of ground state atomic oxygen, $O(^3P)$, with CH_3Br:

$$O + CH_3Br \rightarrow CH_2Br + OH \qquad (6)$$

is nearly thermoneutral and can be expected to possess a significant activation barrier. Three groups (Wilson and O'Donovan, 1968), (Herron and Huie, 1969) and (Westenberg and deHaas, 1975) have measured the rate constant at elevated temperatures (350-1000 K). The most recent NIST evaluation by Herron (1988) recommends:

$$k = 3.3 \times 10^{-11} \exp(-3900/T) \text{ cm}^3/\text{s} \qquad (7)$$

which extrapolates to 1.8×10^{-17} at 270 K. Herron suggests this rate constant has an overall error factor of 3 over the temperature range of 400-1500 K. It may be more uncertain at atmospheric temperatures.

NO_3 Reaction

The reaction of CH_3Br with the nitrate radical has been measured at 298 K in a competitive reaction with toluene by Carlier et al. (1987). The absolute rate depends on the choice of the NO_3 + toluene rate and is quoted as either $(1.57 \pm 0.11) \times 10^{-17}$ or $(3.05 \pm 0.21) \times 10^{-17}$ in Wayne et al. (1990). I estimate a 270°K rate of 1.5×10^{-17} cm^3/s based on this single determination. The reaction products have not been determined, but are probably HNO_3 and CH_2Br.

HO_2 Reaction

Chemical thermodynamic and molecular dynamic considerations suggest that the hydroperoxyl radical will react at a negligible rate with CH_3Br at atmospheric temperatures. A survey of HO_2 kinetics reviews (Lloyd, 1974; Kaufman and Sherwell, 1983) suggests strongly that saturated hydrocarbon or halocarbon compounds are quite unreactive with HO_2.

$O(^1D)$ Reaction

Singlet atomic oxygen, $O(^1D)$, is produced in the photodissociation of atmospheric ozone. While no measurement of its reaction rate with CH_3Br was located in the literature, measurements with CH_3F, CH_3Cl and CF_3Br have been made (Gillespie et al., 1977; Force and Wiesenfeld, 1981) these studies suggest that $O(^1D)$ can react readily with CH_3Br:

$$O(^1D) + CH_3Br \rightarrow CH_2Br + OH \quad (8)$$

$$\rightarrow CH_3 + BrO \quad (9)$$

Based on the reaction rate of 1.9×10^{-10} cm^3/s measured for CH_3Cl (Force and Wiesenfeld, 1981), I estimate a rate for $CH_3Br + O(^1D)$ of 2.0×10^{-10} cm^3/s. $O(^1D)$ reaction rates generally have little or no temperature dependence.

REACTION KINETICS OF ACTIVE BROMINE COMPOUNDS

A few comments on the current state of the reaction kinetics of active stratospheric bromine compounds (Br, BrO, $BrONO_2$, HOBr and HBr) are listed below.

Key reactions probably involve Br + O_3, H_2CO, HO_2; HBr + O and OH and BrO + O, NO, ClO and NO_2(+M). The reaction of BrO with O_3 is not believed to occur at atmospheric temperatures. The photodissociation of $BrONO_2$ and BrO are also of interest. The status of these reactions as reflected in the 1990 NASA evaluation has been assessed and noted below.

Comments on Br Atom Reactions

The NASA 298 K uncertainty factors for the HO_2 and H_2CO reactions with Br are 2.0 and 1.3, respectively. Relatively large temperature dependence uncertainties of -600 ± 600 and -800 ± 200 make these reactions considerably more uncertain at stratospheric temperatures. Br + O_3 is in better, but no great shape (1.2 and -800 ± 200).

Comments on BrO Reactions

BrO + O, NO, and ClO have NASA f(298)'s of 3.0, 1.15 and 1.25, respectively. Their temperature dependent uncertainties are listed as 0 ± 250 and -260 ± 130 for O and NO. The three ClO channels are listed as -430 ± 200 (OClO), -220 ± 200 (ClOO) and -170 ± 200 (BrCl).

The reaction of BrO + HO_2 is quite uncertain, with an f(298) of 3, as are the products, but HOBr is possible. Nothing seems to be known about HOBr photochemistry.

The termolecular reaction of BrO + NO_2 has recently been reinvestigated (Danis, et al., Chem. Phys. Lett. 167, 450-456, 1990). They measured a low pressure limit of k_o at room temperature that is 20% lower than NASA's 1990 evaluation. Their value of n ($k = k_o^{300}\ [T/300]^{-n}$) is also lower (2.0 vs. 3.8 ± 1.0 for NASA). This reaction clearly needs a reevaluation.

Comments on HBr Reactions

The reactions of OH and O with HBr are reasonably well known, with NASA f(298)'s of 1.2 and 1.3, respectively.

Comments on Photolysis Reactions

The BrO photodissociation spectrum is reasonably well known and has been evaluated by NASA (1990).

The $BrONO_2$ cross section has only been measured once, in 1978, and then only at room temperature. The BO + NO_2 + M kinetics suggest the possibility of more than one $BrNO_3$ isomer, so more than on photodissociation cross section may be required. Nothing is known about the $BrONO_2$ photodissociation products. By analogy with $ClONO_2$ a best working guess would be 90% Br + NO_3 and 10% O + $BrNO_2$.

No measurements of HOBr photodissociation properties are presently available.

REFERENCES

Atkinson, R., 1989, "Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds," J. Phys. Chem. Ref. Data, Monograph No. 1.

Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A. and Troe, J., 1989, "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement III, J. Phys. Chem. Ref. Data 18, 881-1097.

Barrie, L.A., Bottenheim, J.W., Schnell, R.C., Crutzen, P.J. and Rasmussen, R.A., 1988, "Ozone Destruction and Photochemical Reactions at Polar Sunrise in the Lower Arctic Atmosphere," Nature 334, 138-141.

Carlier, P., Honnadie, H., Katoudis, A., Martinet, A. and Mouvier, G., 1987, Kinetic Studies Under Simulated Atmospheric Conditions of Nitrate Radical with Various Radicals. In Nielsen O.J. and Cox, R.A. (eds.) Tropospheric NO_x Chemistry-Gas Phase and Multiphase Aspects, Air Pollution Report 9, EUR 11440. CEC, Brussels.

Cohen, N. and Benson, S.W., 1987, "Transition-State-Theory Calculations for Reactions of OH with Haloalkanes," J. Phys. Chem. 91, 162-170.

Davis, D.D., Machando, G., Conaway, B., Oh, Y. and Watson, R., 1976, "A Temperature Dependent Kinetics Study of the Reaction of OH with CH_3Cl, CH_2Cl_2, $CHCl_3$ and CH_3Br," J. Chem. Phys. 65, 1268-1274.

DeMore, W.B., Sander, S.P., Golden, D.M., Molina, M.J., Hampson, R.F., Kurylo, M.J., Howard, C.J. and Ravishankara, A.R., 1990, "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling," Evaluation No. 9, JPL Publication 90-1, Jet Propulsion Laboratory.

Force, A.P. and Wiesenfeld, J.R., 1981, "Collisional Deactivation of $O(^1D_2)$ by the Halomethanes, Direct Determination of Reaction Efficiency," J. Phys. Chem. 85, 782-785.

Gann, R.G., Barnes, J.D., Davis, S., Harris, J.S., Harriss, R.N., Herron, J.T., Levin, B.C., Mopsik, F.I., Notarianni, K.A., Nyden, M.R., Paabo, M. and Ricker, R.E., 1990, "Preliminary Screening Procedures and Criteria for Replacements for Halons 1211 and 1301, NIST Technical Note 1278, National Institute for Standards and Technology.

Gillespie, N.M., Garraway, J. and Donovan, R.J., 1977, "Reaction of $O(^1D_2)$ with Halomethanes," J. Photochem. 7, 29-40.

Gillotay, D. and Simon, P.C., 1988, "Ultraviolet Absorption Cross-Sections of Methyl Bromide at Stratospheric Temperatures," Annual. Geophys. 6, 211-215.

Grogjean, D., 1991, "Atmospheric Chemistry of Toxic Contaminants. 4 Saturated Halogen Aliphatics: Methyl bromide, Epichlorhydrin, Phosgene," J. Air Waste Manage. Assoc. 41, 56-61.

Herron, J.T., 1988, "Evaluated Chemical Kinetic Data for Reactions of Atomic Oxygen $O(^3P)$ with Saturated Organic Compounds in the Gas Phase," J. Phys. Chem. Ref. Data 17, 967-1026.

Herron, J.T. and Huie, R.E., 1973, "Rate Constants for the Reactions of Atomic Oxygen (O^3P) with Organic Compounds in the Gas Phase," J. Chem. Phys. Ref. Data 2, 467-518.

Herron, J.T. and Huie, R.E., 1969, "Rates of Reaction of Atomic Oxygen (O^3P). Experimental Method and Results for some C_1 to C_5 Chloroalkanes and Bromoalkanes," J. Phys. Chem. 73, 1326.

Howard, C.J. and Evenson, K.M., 1976, "Rate Constants for the Reactions of OH with CH_4 and Fluorine, Chlorine and Bromine Substituted Methanes at 296 K," J. Chem. Phys. 64, 197-202.

Kaufman, M. and Sherwell, J., 1983, Prog. Reac. Kinetics 12, 1.

Molina, L.T., Molina M.J. and Rowland, F.S., 1982, "Ultraviolet Absorption Cross Sections of Several Brominated Methanes and Ethanes of Atmospheric Interest," J. Phys. Chem. 86, 2672-2676.

NIST, 1990, NIST Chemical Gas Kinetics Database (Release 2), Standard Reference Data Base 17, National Institute of Standards and Technology.

Prather, M., 1991, "NASA Goddard Institute for Space Studies, private communication.

Prather, M. and Spivakovsky, C.M., 1990, "Tropospheric OH and the Lifetimes of Hydrochlorofluorocarbons," J. Geophys. Res. 95, 18,723-18,729.

Robbins, D.E., 1976, "Photodissociation of Methyl Chloride and Methyl Bromide in the Atmosphere," Geophys. Res. Lett. 3, 213-216 and 757.

Tschuikow-Roux, E. Faraji, F., Paddison, S., Niedzielski, J. and Miyokawa, K., 1988, "Kinetics of Photochlorination of Halogen (F, Cl, Br) Substituted Methanes," J. Phys. Chem. 92, 1488-1495.

Tschuikow-Roux, E. and Paddison, S., 1987, "Bond Dissociation Energies and Radical Heats of Formation in CH_3Cl, CH_2Cl_2, CH_3Br, CH_2Br_2, CH_2FCl and $CHFCl_2$," Int. J. Chem. Kinet. 19, 15-24.

Uthman, A.P., Domlein, P.J., Allston, T.D., Withiam, M.C., McClements, M.J. and Takacs, G.A., 1978, "Photoabsorption Spectra of Gaseous Methyl Bromide, Ethylene Dibromide, Nitrosyl Bromide, Thionyl Chloride and Sulfuryl Chloride," J. Phys. Chem. 82, 2252-2257.

Wayne, R.P. et al., 1990, "The Nitrate Radical: Physics, Chemistry and the Atmosphere," Air Pollution Research Report 31, CEC, Brussels.

Westenberg, A.A. and deHaas, A., 1975, "Reaction Rates of O + CH_3Br and O + CH_3Cl," J. Chem. Phys. 62, 4477-4479.

Wilson, W.E., Jr. and O'Donovan, J.T., 1968, "Rate Constants for the Reaction of Oxygen Atoms with CH_3Cl, CH_3Br and CF_3H," J. Chem. Phys. 48, 2829-.

Wofsy, S.C., McElroy, M.B. and Yung, Y.L., 1975, "The Chemistry of Atmospheric Bromine," Geophys. Res. Lett. 2, 215-218.

Vaghjiani, G.L. and Ravishankara, A.R., 1991, "New Measurement of the Rate Coefficient for the Reaction of OH with Methane," Nature 350, 406-409.

Yung, Y.L., Pinto, I.P., Watson, R.T. and Sander, S.P., 1980, "Atmospheric Bromine and Ozone Perturbations in the Lower Stratosphere," J. Atmos. Sci. 37, 339-353.

Appendix D

Description of the AER one-dimensional photochemical transport model

Results from the AER 1-D model have been described in several publications (Fisher et al, 1990; Rodriguez et al, 1988; Ko and Sze, 1983; Sze and Ko, 1980). The model simulates the vertical distribution of about 50 species interacting through over 150 elementary reactions. The species included in the model are given in table 1. The kinetic data are based on the recommendation of the NASA-JPL panel (DeMore et al, 1990).

The model simulates the vertical distribution of the species by parameterizing transport in terms of a vertical eddy diffusion formalism. It calculates the distributions of the source gases (N_2O, CH_4, organic chlorine species and organic bromine species), the corresponding radical species (oxygen, nitrogen, hydrogen, chlorine and bromine) and ozone, taking into account all the photochemical and radiation couplings and feedbacks among the species. Calculated distributions of the species have been extensively compared to available observations for validation.

While the utility of the 1-D model is somewhat limited by its inability to simulate the latitudinal and seasonal behavior of the trace gases, it remains a useful tool for obtaining first order assessment of various effects. The parallel effort at AER of continuous updating both the 1-D and 2-D models assures us that results from the 1-D model are properly interpreted.

References

DeMore, W.B., S.P. Sanders, D.M. Golden, M.J. Molina, R.F. Hampson, M.J. Kurylo, C.J. Howard, and A.R. Ravishankara (1990) Chemical kinetics and photochemical data for use in stratospheric modeling. *JPL Publication 90-1*, Jet Propulsion Laboratory, Pasadena, CA.

Fisher, D.A., C.H. Hales, D.L. Filkin, M.K.W. Ko, N.D. Sze, P.S. Connell, D.J. Wuebbles, I.S.A. Isaksen and F. Stordal (1990) Ozone depletion potentials for chlorofluorocarbons and possible replacements. *Nature*, 344, 508-512.

Ko, M. K. W., and N. D. Sze (1983) Effect of rate data revisions on stratospheric modeling. *Geophys. Res. Lett.*, 10, 341-344.

Rodriguez, J. M., M. K. W. Ko, and N. D. Sze (1988) Antarctic chlorine chemistry: Possible global implications, *Geophys. Res. Lett.*, 15, 257260.

Sze, N. D., and M. K. W. Ko (1980) Photochemistry of COS, CS2, CH_3SCH_3 and H_2S: Implication for the atmospheric sulfur cycle. *Atmos. Environ.*, 14, 1223.

Table D-1. Summary of Chemical Species Included in AER 1-D Model

Fixed species

M	Bulk air density calculated from ideal gas law
O_2	Set equal to 21% of M
H_2O	Stratospheric values parameterized from the LIMS observation Tropospheric values calculated from seasonally varying relative humidity determined from climatology

Long-lived species

N_2O
CH_4, H_2, CO
CH_3Cl, CH_3CCl_3, CCl_4
CFC-11, CFC-12, HCFCs, HFCs
CF_2O, $CFClO$, CCl_2O
CH_3Br, Halon-1301, Halon-1211
$NOY = N + NO + NO_2 + NO_3 + 2 \times N_2O_5 + HNO_3 + ClNO_3 + HNO_4$
$ClY = Cl + ClO + ClNO_3 + HCl + HOCl + OClO + 2 \times Cl_2O_2$
$BrY = Br + BrO + BrNO_3 + HBr + HOBr + 2 \times Br_2$
$O_x = O + O(^1D) + O_3$

Radical species

Oxygen	O, $O(^1D)$
Hydrogen	H, OH, HO_2, H_2O_2
Methyl	CH_3O_2, CH_2O, CH_3OOH
Nitrogen	N, NO, NO_2, NO_3, N_2O_5, HNO_3, $ClNO_3$, HNO_4
Chlorine	Cl, ClO, $ClNO_3$, HCl, HOCl, OClO, Cl_2O_2
Bromine	Br, BrO, $BrNO_3$, HBr, HOBr, Br_2

DAVID LEE

MTG
ON
26TH

NOAA
202-497-5821
FAX 111 5822
D.A. RAVISHANKARA

(617) 547-6207

Private:
(617) 349-2288

~~DAC SZE~~
DAC SZE

JACK KAY 26 ~~MAR~~ — YES

Mason Solomon. yes

Jon Anderson yes

Ron Grimm - no

sherrywood rowland yes ?? CAN WORK 4-6 on 26th

Mario molina — ~~no~~ YES

DAC SZE - YES

BOB WATSON - YES

EPA — ~~NO~~ — YES DAVID LEE Dow

SINGH — NO industry.

MICK RYLO YES

BOB WATSON YES

A.E.R. NRR

CHEM MANFG. ASSOCIAT.

DEE. KUHN

202-887-1300

U.S. PIRG

(615) 292-4893

~~MIKE~~ RYDA YES

United States Senate

MEMORANDUM

Gary Evans - USDA
Who is concerned
235-9070

TRI CAL INC

FACSIMILE COVER PAGE

DATE: February 19, 1992

DELIVER TO: Mr. Jack Wasko

FROM: Dr. Tom Duafala

SUBJECT: MB Meeting/ February 26

NUMBER OF PAGES, INCLUDING THIS COVER PAGE: 1.

IF THERE IS ANY PROBLEM WITH THIS TRANSMISSION, PLEASE CONTACT SENDER AT ((408) 637-0195. THANK YOU.

OUR FACSIMILE TRANSMISSION NUMBER IS: (408) 637-0273.

Jack:

The following is a list of scientists to be invited to Senator Gore's Methyl Bromide Meeting, February 26th:

James	~~1.~~ Dr. H. Singh	(415) 604-6769	
	~~2.~~ J. H. Park	1637	
	~~3.~~ Ron Prinn,		M.I.T.
	~~4.~~ Dr. Dak Sze	(617) 547-6207	
	~~5.~~ Dr. C. E. Kolb	(508) 663-9500	Aerodyne Research
	6. Dr. Ralph Ross	(202) 720-5015	U.S.D.A.

will come if he can $!!

will come

Best regards

Tom

P.O. BOX 1327 • HOLLISTER, CALIFORNIA 95024-1327 • (408) 637-0195 • FAX (408) 637-0273
1029 RAILROAD ST., CORONA, CA 91720 • (714) 737-6960 • FAX (714) 734-1154
400 CASSERLY RD., WATSONVILLE, CA 95076 • (408) 728-8846 • FAX (408) 728-3140

207-942 1941
1435
JACK in BANGOR

DR. RAVISHANKARA
CALL CET
fr BOB WATSON
CALL PAUL BENSON

U.S.D.A (APHIS)
SCIENCE TECH.
Rm 1630 S. BLD
14th Twn SW
WASH 20250

MOLINA
DEP. OF EAPS, 54-1312
MIT.
CAMB MA
02139
617-253-0354

SEND TO

AIRPORT HILTON BANGOR MAINE

list of scientists to call and invite to next methyl bromide meeting

1. susan solomon -- noaa (you have her number -- boulder colorado)
2. jim anderson -- 617-495-5922
3. jack kay -- pls call bob watson's secretary -- 453-2559 and ask his number
4. sherry rowland --(714-856-6016)
5. ron prinn -- mit -- call their directory
6. mike kurylo - 453-1681
7. mario molina -- mit
8. dr singh (spelling??) nasa aimes -- ask watson's office
9. aron goldman -- univ of denver ---
10. dr. chance(?)
11. dr. traub
12. bob watson

**ALSO NEED TO CALL INDUSTRY TO GET THEM ON A DATE

message TO SCIENTISTS:

1. we had an initial meeting with industry to learn the state of the art of our knowledge re: methyl bromide.

2. senator gore is interested in phasing out methyl bromide in light of recent ozone reports

3. industry's repsonse was that there are too many uncertainties -- we don't know much about methyl bromide

4. industry has had a study done by aer labs. they will make it available to this office; we will make it avail. to you asap.

5. would like you to review and come to a follow up meeting to discuss the aer study and whether we have enough info to proceed.

6. feb. 20 from 12:30-2:30 is a very good time for senator. is this possible

STEVE FEIDEL
FAX 260-6344
TITLE: DEP. DIR GLOB GR DEV.
ADDR.
409 NA 5TH SW.
AW 445
DC.
20460

1 NA
260-
7750

NEWS FROM

U.S. Senator Al Gore

(D - Tennessee) SR 393 Russell Building, Washington, D.C. 20510 (202) 224-4944

DATE_____

TO STEVE SEIDEL

FROM J. WOSKO

PAGES including cover_____

SUBJECT _____

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

Feburary 4 1992

Mr. Steve Seidel
Deputy Director Global Change Division
Environmental Protection Agency
401 M st. S.W. ANR-445 West Tower 739
Washington, D.C. 20460

PHOTOCOPY
MISC. HANDWRITING

Dear Mr. Seidel:

Thank you again for participating in our meeting on methyl bromide. The news delivered yesterday by scientists at NASA headquarters regarding the potentially severe ozone depletion we may experience over North America reaffirms what we really already know -- we are dangerously interfering with our planet's life support systems, and we need to act now to remedy the situation. Our own health and that of our children depends on it.

But, we need to plan our actions judiciously and, therefore, we need to ensure that we are operating on the best information available. In that regard, I wanted to ensure that the follow-up actions agreed to at the meeting are proceeding in a timely fashion. As we left it, industry representatives had agreed to make available to the scientists at the meeting and the representatives of the Environmental Protection Agency copies of the scientific analysis of methyl bromide that was done for them at AER laboratories in Massachussetts. In addition, industry representatives indicated that a report detailing global production and use of methyl bromide would soon be completed and would also be made available to the scientists and agency representatives.

The scientists in turn were to make available to the industry representatives the latest WMO/UNEP International Ozone Trends Assessment Report and to recommend to the industry representatives the most useful reports in the scientific literature on this matter.

As we also agreed, I will convene another meeting on this issue within -- then three weeks, now two weeks -- time. My staff will be in touch immediately to pin down the optimum date. To proceed on this front, however, I will need to receive from the industry representatives immediately a copy of the AER study so that I can distribute it to the larger group of scientists we agreed would be invited to review it.

Again thank you for your time and attention. I look forward to seeing you soon and continuing our work on this very important matter.

Sincerely,

Albert Gore, Jr.
United States Senator

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

January 22, 1992

PHOTOCOPY
MISC. HANDWRITING

Mr. Steve Feidel
Deputy Director Global Change Division
Environmental Protection Agency
401 M st. S.W. ANR-445 West Tower 739
Washington, D.C. 20460

Dear Mr. Feidel

I am quite concerned about the recent finding of the WMO/UNEP Ozone Trends Scientific Assessment Panel that "Methyl bromide is the major source of stratospheric bromine." Methyl bromide is, of course, a potent ozone destroying chemical, and the Assessment report as well as other reports in the scientific literature indicate that emissions of methyl bromide are largely anthropogenic in nature.

I would like to discuss this issue in detail. To that end, I would appreciate it if you could join me for a meeting in my office on January 28 at 12:30. I expect that the meeting continue until approximately 2:30. Important issues include the state of our knowledge on the sources and sinks of methyl bromide; the volume of methyl bromide production and use in the United States and abroad; the principle uses of methyl bromide; and the availability of substitute chemicals. Bob Watson from NASA, Dan Albritton and Susan Solomon from NOAA, your colleague Eileen Clausen, Paul Bergson and several representatives of the methyl bromide manufacturing industry have also been invited to attend.

The latest findings on the rate, extent and duration of ozone depletion send a loud warning that we must move ahead quickly in eliminating the production and use of ozone destroying substances. I therefore very much appreciate your willingness to participate in this discussion. I have included in this letter a copy of draft legislation that I would also like to discuss at our meeting.

Sincerely,

Albert Gore, Jr.
United States Senator

M E M O R A N D U M

DATE:1-23-92

TO:Mr. Steve Feidel

FROM:John H. Wosko

SUBJECT:Methyl Bromide meeting
Re: proposed Legislation not yet ready; will fax as soon as possible.

PAUL BERGSON

FAX # 393-4385

TITLE ELL.

ADD

PH. 393-3740

NEWS FROM

U.S. Senator Al Gore

(D - Tennessee) SR 393 Russell Building, Washington, D.C. 20510 (202) 224-4944

DATE_____

TO PAUL BERGSON

FROM J. WOSKO

PAGES including cover_____

SUBJECT _____

Paul. Pl. dist. to appreciate request

Rep. Stark

202-393-3240

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

Feburary 4 1992

Mr. Paul Bergson
Attorney at Law
Sparber and Associates
1325 Pennsylvania Ave. Suite 500
Washington, D.C. 20004

PHOTOCOPY
MISC. HANDWRITING

Dear Mr. Bergson:

Thank you again for participating in our meeting on methyl bromide. The news delivered yesterday by scientists at NASA headquarters regarding the potentially severe ozone depletion we may experience over North America reaffirms what we really already know -- we are dangerously interfering with our planet's life support systems, and we need to act now to remedy the situation. Our own health and that of our children depends on it.

But, we need to plan our actions judiciously and, therefore, we need to ensure that we are operating on the best information available. In that regard, I wanted to ensure that the follow-up actions agreed to at the meeting are proceeding in a timely fashion. As we left it, industry representatives had agreed to make available to the scientists at the meeting and the representatives of the Environmental Protection Agency copies of the scientific analysis of methyl bromide that was done for them at AER laboratories in Massachussetts. In addition, industry representatives indicated that a report detailing global production and use of methyl bromide would soon be completed and would also be made available to the scientists and agency representatives.

The scientists in turn were to make available to the industry representatives the latest WMO/UNEP International Ozone Trends Assessment Report and to recommend to the industry representatives the most useful reports in the scientific literature on this matter.

As we also agreed, I will convene another meeting on this issue within -- then three weeks, now two weeks -- time. My staff will be in touch immediately to pin down the optimum date. To proceed on this front, however, I will need to receive from the industry representatives immediately a copy of the AER study so that I can distribute it to the larger group of scientists we agreed would be invited to review it.

Again thank you for your time and attention. I look forward to seeing you soon and continuing our work on this very important matter.

Sincerely,

Albert Gore, Jr.
United States Senator

NEWS FROM

U.S. Senator Al Gore

(D - Tennessee) SR 393 Russell Building, Washington, D.C. 20510 (202) 224-4944

DATE [redacted]

TO PAUL BERGSON

FROM J. Wosko

PAGES including cover 3

SUBJECT _____

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

January 22, 1992

Mr. Pual Bergson
Attorney at Law
Sparber and Associates
1325 Pennsylvania Ave. Suite 500
Washington, D.C. 20004

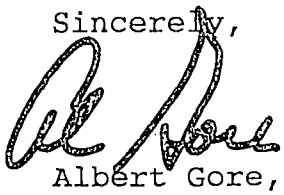
Dear Mr. Bergson

I am quite concerned about the recent finding of the WMO/UNEP Ozone Trends Scientific Assessment Panel that "Methyl bromide is the major source of stratospheric bromine." Methyl bromide is, of course, a potent ozone destroying chemical, and the Assessment report as well as other reports in the scientific literature indicate that emissions of methyl bromide are largely anthropogenic in nature.

I would like to discuss this issue in detail. To that end, I would appreciate it if you could join me for a meeting in my office on January 28 at 12:30. I expect that the meeting continue until approximately 2:30. Important issues include the state of our knowledge on the sources and sinks of methyl bromide; the volume of methyl bromide production and use in the United States and abroad; the principle uses of methyl bromide; and the availability of substitute chemicals. Bob Watson from NASA, Dan Albritton and Susan Solomon from NOAA, Eileen Clausen and Steve Feidel from the Environmental Protection Agency and several representatives of the methyl bromide manufacturing industry have also been invited to attend.

The latest findings on the rate, extent and duration of ozone depletion send a loud warning that we must move ahead quickly in eliminating the production and use of ozone destroying substances. I therefore very much appreciate your willingness to participate in this discussion. I have included in this letter a copy of draft legislation that I would also like to discuss at our meeting.

Sincerely,



Albert Gore, Jr.
United States Senator

M E M O R A N D U M

DATE:1-23-92

TO:Ms. Eileen Clausen

FROM:John H. Wosko

SUBJECT:Methyl Bromide meeting
Re: proposed Legislation not yet ready; will fax as soon as possible.

United States Senate

MEMORANDUM

PUR

WASHINGTON

MOFFETT FIELD

CA 94035

283-3

SUSAN SOLOMON
497-3483
FAX 303-497-5373
TITLE PROG. LDER
MIDDLE
ADD R/E/AL-9

NEWS FROM

U.S. Senator Al Gore

(D - Tennessee) SR 393 Russell Building, Washington, D.C. 20510 (202) 224-4944

DATE_____

TO Susan So Comou

FROM J. Wosko

PAGES including cover_____

SUBJECT _____

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

Feburary 4 1992

Dr. Susan Solomon
Program Leader, Middle Atmosphere Program
NOAA Aeronomy Labortory
R/E/AL - 8 325 Broadway
Boulder, CO. 80303

Dear Dr. Solomon:

Thank you again for participating in our meeting on methyl bromide. The news delivered yesterday by scientists at NASA headquarters regarding the potentially severe ozone depletion we may experience over North America reaffirms what we really already know -- we are dangerously interfering with our planet's life support systems, and we need to act now to remedy the situation. Our own health and that of our children depends on it.

But, we need to plan our actions judiciously and, therefore, we need to ensure that we are operating on the best information available. In that regard, I wanted to ensure that the follow-up actions agreed to at the meeting are proceeding in a timely fashion. As we left it, industry representatives had agreed to make available to the scientists at the meeting and the representatives of the Environmental Protection Agency copies of the scientific analysis of methyl bromide that was done for them at AER laboratories in Massachussetts. In addition, industry representatives indicated that a report detailing global production and use of methyl bromide would soon be completed and would also be made available to the scientists and agency representatives.

The scientists in turn were to make available to the industry representatives the latest WMO/UNEP International Ozone Trends Assessment Report and to recommend to the industry representatives the most useful reports in the scientific literature on this matter.

As we also agreed, I will convene another meeting on this issue within -- then three weeks, now two weeks -- time. My staff will be in touch immediately to pin down the optimum date. To proceed on this front, however, I will need to receive from the industry representatives immediately a copy of the AER study so that I can distribute it to the larger group of scientists we agreed would be invited to review it.

Again thank you for your time and attention. I look forward to seeing you soon and continuing our work on this very important matter.

Sincerely,

Albert Gore, Jr.
United States Senator

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

January 22, 1992

Dr. Susan Solomon
Program Leader, Middle Atmosphere Program
NOAA Aeronomy Labortory
R/E/AL-8 325 Broadway
Boulder CO. 80303

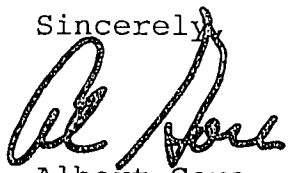
Dear Dr. Solomon

I am quite concerned about the recent finding of the WMO/UNEP Ozone Trends Scientific Assessment Panel that "Methyl bromide is the major source of stratospheric bromine." Methyl bromide is, of course, a potent ozone destroying chemical, and the Assessment report as well as other reports in the scientific literature indicate that emissions of methyl bromide are largely anthropogenic in nature.

I would like to discuss this issue in detail. To that end, I would appreciate it if you could join me for a meeting in my office on January 28 at 12:30. I expect that the meeting continue until approximately 2:30. Important issues include the state of our knowledge on the sources and sinks of methyl bromide; the volume of methyl bromide production and use in the United States and abroad; the principle uses of methyl bromide; and the availability of substitute chemicals. Bob Watson from NASA, your colleague Dan Albritton, Eileen Claussen and Steve Feidel from the Environmental Protection Agency, and several representatives of the methyl bromide manufacturing industry have also been invited to attend.

The latest findings on the rate, extent and duration of ozone depletion send a loud warning that we must move ahead quickly in eliminating the production and use of ozone destroying substances. I therefore very much appreciate your willingness to participate in this discussion. I have included in this letter a copy of draft legislation that I would also like to discuss at our meeting.

Sincerely,



Albert Gore, Jr.
United States Senator

M E M O R A N D U M

DATE:1-23-92

TO:Dr. Albritton and Dr. Solomon

FROM:John H. Wosko

SUBJECT:Methyl Bromide meeting
Re: proposed Legislation not yet ready; will fax as soon as possible.
Re: Mr. Paul Bergson, Att. will be organizing industry reps.

NEWS FROM

U.S. Senator Al Gore

(D - Tennessee) SR 393 Russell Building, Washington, D.C. 20510 (202) 224-4944

DATE_____

TO Dr. A. RAVISHANKAR

FROM J. WOSKO

PAGES including cover 1

SUBJECT _____

NEWS FROM

U.S. Senator Al Gore

(D - Tennessee) SR 393 Russell Building, Washington, D.C. 20510 (202) 224-4944

DATE _____

TO Dr. M. MOLINA

FROM J. WOSKO

PAGES including cover 1

SUBJECT _____

M E M O R A N D U M

DATE: February 20, 1992

TO: Methyl Bromide meeting participants

FROM: Jack Wosko

SUBJECT: The meeting on the 26th of February, from 4:00 to 6:00 pm. will be held in room 189 of the Russell Senate Office Building. (same bldg as Senator Gore's office).

United States Senate

MEMORANDUM

David Lee

ADR - 445 West Tower 239

401 Mass S.W

D.C. 20460

260-1497

260-2040

United States Senate

MEMORANDUM

A M.

ARE

R/E/AL 2.

BOB T. WATSON

FAX: 755-5032 (202)

TITLE: ORB. PROCESS STUDIES
PROOF.

ADD:

NASA

S.E.P 600 HOUSE

S.W.

20546

NEWS FROM

U.S. Senator Al Gore

(D - Tennessee) SR 393 Russell Building, Washington, D.C. 20510 (202) 224-4944

DATE _____

TO Bob Watson

FROM J. Wosko

PAGES including cover _____

SUBJECT _____

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

Feburary 4 1992

Dr.Robert Watson
Director of Process Studies Program Office
NASA Headquarters
S.E.P. 600 Independence Ave. S.W.
Washington, D.C. 20546

Dear Dr. Watson:

Thank you again for participating in our meeting on methyl bromide. The news delivered yesterday by scientists at NASA headquarters regarding the potentially severe ozone depletion we may experience over North America reaffirms what we really already know -- we are dangerously interfering with our planet's life support systems, and we need to act now to remedy the situation. Our own health and that of our children depends on it.

But, we need to plan our actions judiciously and, therefore, we need to ensure that we are operating on the best information available. In that regard, I wanted to ensure that the follow-up actions agreed to at the meeting are proceeding in a timely fashion. As we left it, industry representatives had agreed to make available to the scientists at the meeting and the representatives of the Environmental Protection Agency copies of the scientific analysis of methyl bromide that was done for them at AER laboratories in Massachussetts. In addition, industry representatives indicated that a report detailing global production and use of methyl bromide would soon be completed and would also be made available to the scientists and agency representatives.

The scientists in turn were to make available to the industry representatives the latest WMO/UNEP International Ozone Trends Assessment Report and to recommend to the industry representatives the most useful reports in the scientific literature on this matter.

As we also agreed, I will convene another meeting on this issue within -- then three weeks, now two weeks -- time. My staff will be in touch immediately to pin down the optimum date. To proceed on this front, however, I will need to receive from the industry representatives immediately a copy of the AER study so that I can distribute it to the larger group of scientists we agreed would be invited to review it.

Again thank you for your time and attention. I look forward to seeing you soon and continuing our work on this very important matter.

Sincerely,

Albert Gore, Jr.
United States Senator

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

January 22, 1992

PHOTOCOPY
MISC. HANDWRITING

Dr. Robert Watson
Director of Process Studies Program Office
NASA Headquarters
S.E.P. 600 Independence ave. S.W.
Washington, D.C. 20546

Dear Dr. Watson:

I am quite concerned about the recent finding of the WMO/UNEP Ozone Trends Scientific Assessment Panel, of which you are a co-chair, that "Methyl bromide is the major source of stratospheric bromine." Methyl bromide is, of course, a potent ozone destroying chemical, and the Assessment report as well as other reports in the scientific literature indicate that emissions of methyl bromide are largely anthropogenic in nature.

I would like to discuss this issue in detail. To that end, I would appreciate it if you could join me for a meeting in my office on January 28 at 12:30. I expect that the meeting continue until approximately 2:30. Important issues include the state of our knowledge on the sources and sinks of methyl bromide; the volume of methyl bromide production and use in the United States and abroad; the principle uses of methyl bromide; and the availability of substitute chemicals. Dan Albritton and Susan Solomon from NOAA's Aeronomy Lab, Eileen Claussen and Steve Feidel from the Environmental Protection Agency, and several representatives of the methyl bromide manufacturing industry have also been invited to attend.

The latest findings on the rate, extent and duration of ozone depletion send a loud warning that we must move ahead quickly in eliminating the production and use of ozone destroying substances. I therefore very much appreciate your willingness to participate in this discussion. I have included in this letter a copy of draft legislation that I would also like to discuss at our meeting.

Sincerely,

Albert Gore, Jr.
United States Senator

M E M O R A N D U M

DATE:1-23-92

TO:Dr. Robert Watson

FROM:John H. Wosko

SUBJECT:Methyl Bromide meeting
Re: proposed Legislation not yet ready; will fax as soon as possible.
Re: Mr. Paul Bergson, Att. will be organizing industry reps.

Tom Duatala + Monday or Wednesday;

= AER Laboratories

- one-step away from being finalized
- funded by Methyl Bromide Assocs of U.S, EC, & Japan.

- perhaps as soon as monday;

Dr. Singh is in India right now: will return around March / Moffet Field NASA Ames Research: Industry:

soil fumigant: used for the control of insects; nematodes; plant diseases eg. bacteria;

U.S. plant quarantine program:
also eg. for interstate shipments of some commodities;

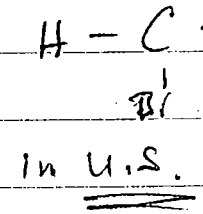
also used for stored grains: $CH_3Br \Rightarrow CH_3^+ Br^-$

also used as a soil fumigant; // 40 or 50 years;

- registration standard:
- FIFRA:

pre-plant treatment: // about 1/3 of all use is in U.S.

acutely toxic: CH_4



United States Senate

MEMORANDUM

DAC SZE

AER LABS

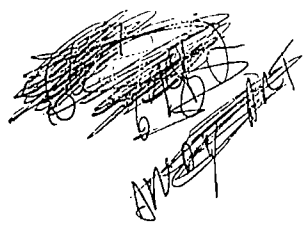
617-547-6207

AER INC.
840 MEMORIAL DR
CAMBRIDGE
~~CAMB~~ MA. 02139

United States Senate

MEMORANDUM

JACK KAY
NASA - BUREAU ROOM CRWD
MICHAEL KURYLO
~~TIM ANDERSON~~
IN BANGOR ME
NASA OZONE PROJECT
BANGOR INT'L AIRPORT
287 GODFREY
BANGOR ME 04401
ATT: JIM
DOCK 11



Dan Albritton

FAX # 303-499-5373

TITLE Dir. Road
AERO Mgr

ADDRESS
325 Broadway
Boulder, Co.
80303

NEWS FROM

U.S. Senator Al Gore

(D - Tennessee) SR 393 Russell Building, Washington, D.C. 20510 (202) 224-4944

DATE_____

TO DAN ALBRITTON

FROM J. WOSKO

PAGES including cover_____

SUBJECT _____

303 - 497
5785

OR.
OR.

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

Feburary 4 1992

Dr. Daniel Albritton
Director NOAA Aeronomy Labortory
NOAA Aeronomy Labortory
R/E/AL 325 Broadway
Boulder, CO. 80303

Dear Dr. Aldritton:

Thank you again for participating in our meeting on methyl bromide. The news delivered yesterday by scientists at NASA headquarters regarding the potentially severe ozone depletion we may experience over North America reaffirms what we really already know -- we are dangerously interfering with our planet's life support systems, and we need to act now to remedy the situation. Our own health and that of our children depends on it.

But, we need to plan our actions judiciously and, therefore, we need to ensure that we are operating on the best information available. In that regard, I wanted to ensure that the follow-up actions agreed to at the meeting are proceeding in a timely fashion. As we left it, industry representatives had agreed to make available to the scientists at the meeting and the representatives of the Environmental Protection Agency copies of the scientific analysis of methyl bromide that was done for them at AER laboratories in Massachussetts. In addition, industry representatives indicated that a report detailing global production and use of methyl bromide would soon be completed and would also be made available to the scientists and agency representatives.

The scientists in turn were to make available to the industry representatives the latest WMO/UNEP International Ozone Trends Assessment Report and to recommend to the industry representatives the most useful reports in the scientific literature on this matter.

As we also agreed, I will convene another meeting on this issue within -- then three weeks, now two weeks -- time. My staff will be in touch immediately to pin down the optimum date. To proceed on this front, however, I will need to receive from the industry representatives immediately a copy of the AER study so that I can distribute it to the larger group of scientists we agreed would be invited to review it.

Again thank you for your time and attention. I look forward to seeing you soon and continuing our work on this very important matter.

Sincerely,

Albert Gore, Jr.
United States Senator

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

January 22, 1992

PHOTOCOPY
MISC. HANDWRITING

Dr. Daniel Albritton
Director NOAA Aeronomy Labortory
NOAA Aeronomy Labortory
R/E/AL 325 Broadway
Boulder CO. 80303

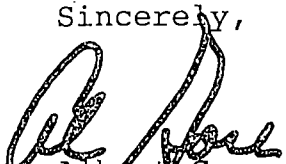
Dear Dr. Albritton

I am quite concerned about the recent finding of the WMO/UNEP Ozone Trends Scientific Assessment Panel, of which you are a co-chair, that "Methyl bromide is the major source of stratospheric bromine." Methyl bromide is, of course, a potent ozone destroying chemical, and the Assessment report as well as other reports in the scientific literature indicate that emissions of methyl bromide are largely anthropogenic in nature.

I would like to discuss this issue in detail. To that end, I would appreciate it if you could join me for a meeting in my office on January 28 at 12:30. I expect that the meeting continue until approximately 2:30. Important issues include the state of our knowledge on the sources and sinks of methyl bromide; the volume of methyl bromide production and use in the United States and abroad; the principle uses of methyl bromide; and the availability of substitute chemicals. Bob Watson from NASA, your colleague Susan Solomon, Eileen Claussen and Steve Feidel from the Environmental Protection Agency, and several representatives of the methyl bromide manufacturing industry have also been invited to attend.

The latest findings on the rate, extent and duration of ozone depletion send a loud warning that we must move ahead quickly in eliminating the production and use of ozone destroying substances. I therefore very much appreciate your willingness to participate in this discussion. I have included in this letter a copy of draft legislation that I would also like to discuss at our meeting.

Sincerely,



Albert Gore, Jr.
United States Senator

EILEEN CLAUSEN

FAX# 260-7991

TITLE: DIR OF ATMOSPHERIC INDOOR AIR PROGRAMS

ADD

NEWS FROM

U.S. Senator Al Gore

(D - Tennessee) SR 393 Russell Building, Washington, D.C. 20510 (202) 224-4944

DATE_____

TO EILEEN CLAUSEN

FROM J. WOSKO

PAGES including cover_____

SUBJECT _____

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

Feburary 4 1992

Ms. Eileen Clausen
Director of Atmosphere and Indoor Air Program
Environmental Protection Agency
401 M st. S.W. ANR-445 West Tower 739
Washington, D.C. 20460

Dear Ms. Clausen:

Thank you again for participating in our meeting on methyl bromide. The news delivered yesterday by scientists at NASA headquarters regarding the potentially severe ozone depletion we may experience over North America reaffirms what we really already know -- we are dangerously interfering with our planet's life support systems, and we need to act now to remedy the situation. Our own health and that of our children depends on it.

But, we need to plan our actions judiciously and, therefore, we need to ensure that we are operating on the best information available. In that regard, I wanted to ensure that the follow-up actions agreed to at the meeting are proceeding in a timely fashion. As we left it, industry representatives had agreed to make available to the scientists at the meeting and the representatives of the Environmental Protection Agency copies of the scientific analysis of methyl bromide that was done for them at AER laboratories in Massachussetts. In addition, industry representatives indicated that a report detailing global production and use of methyl bromide would soon be completed and would also be made available to the scientists and agency representatives.

The scientists in turn were to make available to the industry representatives the latest WMO/UNEP International Ozone Trends Assessment Report and to recommend to the industry representatives the most useful reports in the scientific literature on this matter.

As we also agreed, I will convene another meeting on this issue within -- then three weeks, now two weeks -- time. My staff will be in touch immediately to pin down the optimum date. To proceed on this front, however, I will need to receive from the industry representatives immediately a copy of the AER study so that I can distribute it to the larger group of scientists we agreed would be invited to review it.

Again thank you for your time and attention. I look forward to seeing you soon and continuing our work on this very important matter.

Sincerely,

Albert Gore, Jr.
United States Senator

ALBERT GORE, JR.
TENNESSEE

393 RUSSELL SENATE OFFICE BUILDING
PHONE: 202-224-4944

United States Senate

WASHINGTON, DC 20510-4202

January 22, 1992

Ms. Eileen Clausen
Director of Atmosphere and Indoor Air Program
Environmental Protection Agency
401 M st. S.W. ANR-445 West Tower 739
Washington, D.C. 20460

Dear Ms. Clausen

I am quite concerned about the recent finding of the WMO/UNEP Ozone Trends Scientific Assessment Panel that "Methyl bromide is the major source of stratospheric bromine." Methyl bromide is, of course, a potent ozone destroying chemical, and the Assessment report as well as other reports in the scientific literature indicate that emissions of methyl bromide are largely anthropogenic in nature.

I would like to discuss this issue in detail. To that end, I would appreciate it if you could join me for a meeting in my office on January 28 at 12:30. I expect that the meeting continue until approximately 2:30. Important issues include the state of our knowledge on the sources and sinks of methyl bromide; the volume of methyl bromide production and use in the United States and abroad; the principle uses of methyl bromide; and the availability of substitute chemicals. Bob Watson from NASA, Dan Albritton and Susan Solomon from NOAA, your colleague Steve Feidel, Paul Bergson and several representatives of the methyl bromide manufacturing industry have also been invited to attend.

The latest findings on the rate, extent and duration of ozone depletion send a loud warning that we must move ahead quickly in eliminating the production and use of ozone destroying substances. I therefore very much appreciate your willingness to participate in this discussion. I have included in this letter a copy of draft legislation that I would also like to discuss at our meeting.

Sincerely,

Albert Gore, Jr.
United States Senator

M E M O R A N D U M

DATE:1-23-92

TO:Ms. Eileen Clausen

FROM:John H. Wosko

SUBJECT:Methyl Bromide meeting
Re: proposed Legislation not yet ready; will fax as soon as possible.

January 22, 1992

Dr. Robert Watson

NASA Headquarters
Washington, D.C.

Dear Dr. Watson:

I am quite concerned about the recent finding of the WMO/UNEP Ozone Trends Scientific Assessment Panel, of which you are a co-chair, that "Methyl bromide is the major source of stratospheric bromine." Methyl bromide is, of course, a potent ozone destroying chemical, and the Assessment report as well as other reports in the scientific literature indicate that emissions of methyl bromide are largely anthropogenic in nature.

I would like to discuss this issue in detail. To that end, I would appreciate it if you could join me for a meeting in my office on January 28 at 12:30. I expect that the meeting continue until approximately 2:30. Important issues include the state of our knowledge on the sources and sinks of methyl bromide; the volume of methyl bromide production and use in the United States and abroad; the principle uses of methyl bromide; and the availability of substitute chemicals. Dan Albritton and Susan Solomon from NOAA's Aeronomy Lab, Eileen Claussen from the Environmental Protection Agency, and several representatives of the methyl bromide manufacturing industry have also been invited to attend.

The latest findings on the rate, extent and duration of ozone depletion send a loud warning that we must move ahead quickly in eliminating the production and use of ozone destroying substances. I therefore very much appreciate your willingness to participate in this discussion. I have included in this letter a copy of draft legislation that I would also like to discuss at our meeting.

Sincerely,

Albert Gore, Jr.
United States Senator

TO: Katie McGinty
FROM: Cornelia Burr
DATE: January 29, 1992
RE: CAB92.020

Here are a few comments to accompany the draft for the phase out language:

(1) The language in the instructions concerning production or consumption was changed to "manufactured, processed, or used" to key to existing definitions under the Emergency Planning and Community Right-to-Know Act of 1986. This meets your intent to cover the full spectrum of handling the chemical. Consumption could be read to imply that the chemical is used up. A broader range of possibilities exists.

(2). The exception in the instructions looks as if you intended a waiver process, whereby the Administrator makes a determination whether or not to allow a use or activity. The instructions were so broadly written as to allow for a loophole you do not intend. Each specific use may not directly destroy the stratospheric ozone layer. The aggregate effect of such uses could have a significant effect. Therefore, this draft is written in terms of whether the use contributes to the destruction of the stratospheric ozone layer, rather than whether the use directly destroys it.

Please do not hesitate to call if you have any questions. I marked this draft as a discussion draft so that you may review it to see if it meets your intent.

102D CONGRESS
2D SESSION

S. _____

IN THE SENATE OF THE UNITED STATES

Mr. GORE introduced the following bill; which was read twice and referred to the Committee on _____

A BILL

Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled,

SECTION. 1.

The Congress finds that:

(1) Ozone in the stratospheric layer of the atmosphere (hereafter referred to as "stratospheric ozone") protects all living things from harmful ultraviolet radiation from the sun, and has been significantly depleted over almost every geographic area of the Earth because of the effect of air pollution containing certain halogenated chemicals.

(2) Recently the International Ozone Trends Scientific Assessment Panel of the United Nations Environment Program and the World Meterological Organization reported that the depletion of stratospheric ozone is occurring at a rate that is twice the rate that had previously been measured or predicted, and that even during summer months stratospheric ozone continues to be significantly depleted.

(4) The findings described in paragraphs (1) through (3) necessitate a reappraisal of national and international policies concerning the control of chemicals that contribute to the depletion of the stratospheric ozone.

(5) Bromine in the stratospheric layer of the atmosphere (hereafter referred to as "stratospheric bromine") is estimated to be 30 to 120 times more efficient than chlorine with respect to causing the destruction of stratospheric ozone, and the major source of stratospheric bromine is methyl bromide.

(6) Methyl bromide is not currently regulated under the Clean Air Act or the Act entitled "An act to amend the Clear Air Act to provide for the establishment of health protective national ambient air quality standards, and for other purposes" (com-

monly known as the Clean Air Act Amendments of 1990).

(7) Reductions in emissions of methyl bromide would contribute effectively to the restoration of ozone in the stratospheric layer.

SEC. 2. PHASE-OUT OF METHYL BROMIDE.

(a) IN GENERAL.-Title VI of the Clean Air Act (42 U.S.C. 7671 et seq.) is amended by adding at the end of the title the following new section:

"PHASE-OUT OF METHYL BROMIDE

"SEC. 619. (a) IN GENERAL.—Except as provided in subsection (b), it shall be unlawful to manufacture, process, or use methyl bromide, or import methyl bromide into the United States for processing or use.

"(b) WAIVERS.—(1) The Administrator may waive the requirements of subsection (a), if—

"(A) a person submits an application (in such form and manner as the Administrator shall prescribe by regulation) for a waiver under this subsection to the Administrator; and

"(B) on the basis of the information in the application, the Administrator determines that the use of the methyl bromide that is the subject of the waiver will not contribute to the destruction of stratospheric ozone.

"(2) The Administrator may attach such conditions to a waiver under this subsection as the Administrator determines to be appropriate.

"(c) MANUFACTURE, PROCESS, DEFINED.—For the purposes of this section—

"(1) the term 'manufacture' has the meaning given by section 313(b)(1)(C)(i) of the Emergency Planning and Community Right-To-Know Act of 1986 (42 U.S.C. 11023(b)(1)(C)(i)); and

(2) the term 'process' has the meaning given by section 313(b)(1)(C)(ii) of such Act (42. U.S.C. 11023(b)(1)(C)(ii)).

"(d) EFFECTIVE DATE.—The provisions of this section shall become effective on January 1, 1996.".

NEWS FROM

U.S. Senator Al Gore

(D - Tennessee) SR 393 Russell Building, Washington, D.C. 20510 (202) 224-4944

DATE _____

TO Susan / Bob

FROM Katie

PAGES including cover 9

SUBJECT _____

Pls. fax to 303-497-5373
Susan Slaman &
Bob Watson
202-755-5032

This is draft memo I will give to Al on this. Please let me know if this is in the ballpark or if anything needs to be changed.

Thanks!

DRAFT

M E M O R A N D U M

DATE: January 28, 1992

TO: Al

FROM: Katie

SUBJECT: Methyl Bromide meeting

****

Who will be here:

- o Bob Watson (NASA)
- o Susan Solomon (NOAA)
- o Eileen Claussen (EPA)
- o Steve Seidel (EPA)
- o Paul Bergson (an attorney who represents the methyl bromide industry on ozone issues)
- o Tom Dufala (Trical director of research)
- o

Objective: The goal is to make a solid case that the production and use of methyl bromide (CH3Br) should be phased out in short order. Each of the participants in this discussion has received a copy of the draft bill (attached), and therefore knows that you propose to ban ch3br as of january 1, 1996.

Industry Arguments Against: In addition to the usual moaning and wailing, I anticipate the following: They will attack the sufficiency of our knowledge of the bromine budget -- what are the principle sources of atmospheric bromine?; even if CH3Br is a primary source of atmospheric bromine, does the CH3Br derive primarily from natural or anthropogenic sources; does CH3Br-derived bromine directly contribute to ozone loss -- i.e., does the CH3Br make it to the stratosphere to deliver its bromine payload, and if so, is the bromine found in active form (BrO) or is it held in a nonreactive sink (HBr)?; CH3Br is an essential agricultural product and we have no suitable substitutes.

NOTE THAT THEY MAY MENTION THAT THEY INTEND TO ESTABLISH A TWO MILLION RESEARCH EFFORT TO ENHANCE OUR UNDERSTANDING OF THE BROMINE BUDGET. DON'T BUY THIS. WE HAVE SUFFICIENT KNOWLEDGE OF THE BUDGET TO JUSTIFY ACTION NOW, AND (AS I WILL DISCUSS FURTHER BELOW), THE OFFER IS A STALL TACTIC.

Bottom Line: It is true that we do not understand bromine chemistry as well as chlorine chemistry, however, we have evidence sufficient to counter the arguments relating to the bromine budget. The question of substitutes is a tougher one. For some of its uses, namely as a space and commodity fumigant, I have come across promising substitutes. For other uses, namely as a soil fumigant and fungicide and nematicide, the alternatives are not as apparant. However, on this score your message should be that industry should sink its 2 million not into further atmospheric chemistry research, but into finding safe substitute substances and/or processes.

Background on Methyl Bromide:

This sh*t is ubiquitous:

First introduced as an insecticide in 1932. Now used widely as a fumigant for all types of dry foodstuffs, especially produce contained in bags or packages ("commodity fumigant"). It is also used in mills, warehouses, ships, and frieght cars ("structural fumigant"); in greenhouses and fields for the control of nematodes, fungi, and weeds ("soil fumigant"). There are some 87 raw agricultural commodities on the list of foodstuffs that may legally be treated with ch3br, including 13 kinds of nuts, 10 kinds of grains, 36 kinds of vegetables, 19 kinds of fruits as well as every conceivable variety of processed foods. Moreover, USDA requires its use as a fumigant on a wide variety of imported fruits and vegetables as a condition of their entry into the US.

There also are non-ag uses, including industrial applications as a disinfectant, methylating agent and degreaser. Also used as a fire extinguisher (don't know if this use continues, as according to one article: "Originally, they used it in fire extinguishers, ... until they noticed certain people dropping dead whent they extinguished fires in closed spaces.")

SEE ATTACHED MAP OF USAGE IN THE UNITED STATES. NOTE THAT TENNESSEE IS A HEAVY USER. (Also note, curiously, that bread basket states do not rely on it).

This sh*t is nasty:

CH3Br is listed under the Toxic Chemical Release Inventory of the Community Right To Know Act as one of approximately 300 chemicals regarded as "acutely toxic, possible carcinogenic, or capable of having a significant adverse effect on the environment." According to a 1990 Buzzworm article methyl bromide is "an extremely hazardous poison -- a poison with no known antidote, capable of

causing symptoms ranging form headaches, vomiting and vertigo to psychosis, convulsions, delirium, respiratory failure and central nervous system depression resulting in death."

The most authoritative statement on the toxicology and carcinogenesis is Health and Human Service's 1990 National Toxicology Program report:

o it's toxic...."Short-term toxicity tests conducted in various species have shown that methyl bromide is highly toxic to mammals." Moreover, "serious exposure can occur without warning" because "methyl bromide has little odor at potentially toxic concentrations," and because methyl bromide is "extremely penetrating," "standard protective clothing did little to prevent exposure in fumigation operations".

o it's mutagenic...."exposure by inhalation of methyl bromide gas resulted in a significant increase in sex-linked lethal mutations in the germ cells" of male flies.

o it's lethal...."At least 115 known fatalities and 843 known systemic, skin, eye, and other injuries have resulted form methyl bromide exposure." (On this point see also Casarett and Doull's Toxicology: "methyl bromide is said to have been responsible for more deaths in recent years among occupationally exposed persons in California than all of the more publicized organophosphate group of insecticides").

o it's also controversial....

carcinogenic??

A Dutch government study startled EPA and NIH when it found that, in just 90 days, methyl bromide fed to rats produced cancerous tumors. NIH scientists subsequently reviewed the slides used in the Dutch study and concluded that the Dutch had misinterpreted them. According to the US researchers, what the rats developed were "hyperplastic lesions of the forestomach", not carcinoma. But, either way the news ain't good -- such "hyperplastic responses are usually characteristic of carcinogenic chemicals," and the lesions are often forerunners of carcinoma. Moreover, the Dutch suspect that the real reason US criticized their results was because EPA in 1983 had to place ethylene dibromide, a fumigant used for many of the same purposes as methyl bromide, under an emergency ban when it was discovered -- contrary to earlier EPA assurances -- to be a strong carcinogen. I do not know what has been done since the Dutch study to resolve this question.

food residues??

Despite its acute toxicity and ubiquitous use, testing for ch3br residues in foodstuffs is not required (at least as of the writing of the Buzzworm article of March/April 1990). Why? Because, since it is used in gaseous form, it was assumed that none would persist to be absorbed by foodstuffs. The lid was blown on this idea, however, in the mid-1980's when, under a USDA quarantine program, methyl bromide residues were detected in California nuts and Florida citrus. And it is known that methyl bromide is very soluble in fats, so products containing high oil and fatty acid, such as nuts and cheese are likely to retain it. Nonetheless, the largest mfgrs of methyl bromide (Great Lakes Chemical Company and Ethyl Corp.) claim that they do test and have found no detectable levels of methyl bromide. Note here that, even if EPA decided to require such tests, it would be dependent on industry-submitted data.

Ozone Depletion:

From the recent 1991 UNEP/WMO International Ozone Trends Scientific Assessment:

"Stratospheric bromine is 30 - 120 times more efficient than stratospheric chlorine in destroying ozone on a per atom basis."

"Methyl bromide is the major contributor to stratospheric bromine (15pptv). The sources of methyl bromide are not well characterized; however, significant anthropogenic emissions have been suggested."

"If the anthropogenic sources of methyl bromide are significant and their emissions can be reduced, then each 10% reduction in methyl bromide would rapidly result in a decrease in strratospheric bromine of 1.5 pptv, which is equivalent to a reduction in stratospheric chlorine of 0.045 to 0.18 ppbv. This gain is comparable to that of a three-year acceleration of the scheduled phase-out of the CFCs.

Ozone Depletion Potential

Susan Solomon is a lead author of the chapter of the International Assessment dealing with ODPs. The best consensus is that the steady state ODP for ch3br is 0.6.

Susan emphasizes that this is a conservative value. "Steady states" values are determined on the basis of the amount of ozone depletion the substance in question would cause over a 100 year lifetime. CH3Br, however, is a very

short-lived species -- 1-2 years. If instead we look at its ozone depletion potential over that time horizon, the extremely acute impact of ch3br on ozone becomes clear: "Note that although CH3Br displays a relatively small ODP over long time horizons, it has a very large ODP for short time scales by virtue of its short lifetime and the large value of [its ozone depletion efficiency relative to chlorine]." The implication is that controls on CH3Br will have significant, immediate impact on reducing the atmospheric concentration of ozone destructive substances.

Regulatory Implication and Your Legislation:

Pursuant to the Clean Air Act, EPA is required to list any substance with an ODP of 0.2 or greater as a Class I substance -- that is, as an ozone destroyer that will be completely phased out by 2000.

You must be careful to make clear to industry that you are not proposing new legislation because it is your opinion that EPA currently does not have authority to regulate ch3br and therefore new legislation is necessary. To the contrary, now that the ODP determination has been made, EPA does have that authority and in fact is required to act. The point of your legislation is not to establish EPA authority under Clean Air, but rather, to force EPA to go even further and faster than Clean Air permits.

What is the rationale for making EPA move faster??

First, the Parties to the Montreal Protocol in the next year will meet to decide on an accelerated phaseout schedule. Indications are that substances that would be considered "Class I" chemicals under Clean Air -- as ch3br now will be considered -- will be phased out by 1996 under the amendments that likely will be proposed. Therefore, you simply jump start the process and direct that that be the phaseout date for methylbromide. This is a favor to industry -- it's gonna happen anyway and you provide them with "regulatory certainty"....

Second, regardless of what occurrs internationally, the significant short term gains that can be had from ch3br regulation argue for an expedited process. If instead we wait for regulation pursuant to the current terms of the Clean Air Act, the process, involving public notice and hearings could be quite protracted.

Industry Response

Industry therefore knows there's trouble in paradise for them. (Meanwhile nematoids across the country are celebrating...). That does not mean however that they are prepared to raise the white flag. To the contrary, industry plans to fight the Clean Air Class I listing on the grounds that our knowledge of the bromine budget is insufficient, and consequently, the ch3br ODP determination is unsound. Also as indicated above, industry's game will be to propose a 2 million research effort to get a better handle on the chemistry (and to postpone immediate action).

Response to Industry Criticisms

o Is methyl bromide a significant source of atmospheric bromine?

As indicated above, the International Assessment states that methyl bromide is the major contributor to stratospheric bromine.

In addition, Anderson states in a 1989 article in Nature: Salawitch et al. "conclude that the total organic bromine source is between 6 and 20 pptv, with 3 pptv being the man-made perhalogenated bromine gases CF3Br and CF2BrCl, and the rest being methyl bromide".

o Even if methyl bromide is a significant source of atmospheric bromine, what proof is there that there is a significant anthropogenic contribution to atmospheric concentrations?

Industry will bolster this point by noting -- correctly -- that the oceans are a major natural source of CH3Br. In addition, industry also argues that its use of methyl bromide does not contribute to atmospheric concentrations because it gets degraded by soil microbes when it is injected into the ground. Taking each of these points in turn:

Ocean contribution:

Again, the international assessment said "significant anthropogenic emissions have been suggested." In addition, in a 1985 letter to Nature, Penkett et al. reported that "the weight of the evidence does not favor a large natural source [of ch3br. Rather], Our interpretation of the data ... suggests that the predominant source of CH3Br in the atmosphere is anthropogenic rather than natural."

I am unaware of any other natural terrestrial sources of CH3Br. And Grosjean reports in a 1991 article in J. Air

Waste Manage. Assoc. that "There are no reactions by which methyl bromide may form in the atmosphere."

Soil Degradation:

Because CH3Br has C-H bonds, it is possible that bugs would eat it. I am unaware of any evidence demonstrating this, however.

Moreover, as noted above, direct injection into soil is only one of the uses of CH3Br. As indicated, there are significant non-agricultural uses. And even for the agricultural uses, methyl bromide is used as a space and commodity fumigant as well as a soil fumigant. When blasted into silos or on commodities, methyl bromide of course escapes into the atmosphere. Indeed it must be vented into the atmosphere because, since it is acutely toxic, humans could not enter premises where it has been used unless the premises had been fully aired. Venting is standard practice, and it has often been specifically because venting was not done thoroughly enough that humans have been killed -- sometimes instantly -- from exposure. Methyl bromide has a tendency to hide in "pockets" like bathrooms, drawers and other close spaces and therefore is not always fully flushed out in the venting process. Now that CH3Br is being used to fumigate homes and restaurants, etc. people have been killed when they encountered these lingering pockets.

o Even if anthropogenically-derived CH3Br is a major source of atmospheric bromine, how do we know that it makes it up to the stratosphere to deliver its bromine payload?

CALL CICERONE

To refer to Anderson's 1989 Nature article again, he cites Salawitch et al. for the proposition that 6-20 pptv of inorganic bromine is delivered to the "lower stratosphere" by organic gases, and primarily by CH3Br.

In addition, Grosjean states that: "Methyl bromide is one of the least reactive toxic air contiminants, with a correspondingly long persistence in the atmosphere. Reactions with O3 and NO3 are negligibly slow. Photolysis is a negligible removal process for CH3Br in the lower troposphere. Methyl bromide reacts only slowly with the hydroxyl radical." Therefore, ch3br survives the reactions that cleanse many other substances out of the troposphere. It therefore likely persists and makes its way into the stratosphere. As Grosjean continues: "Upward diffusion and deposition are thus the dominant loss processes for CH3Br in the troposhere."

o Even if the bromine does get delivered to the stratosphere, does the bromine then destroy ozone?

The question here is whether the bromine in the stratosphere is in active form (BrO) or is trapped in a reservoir such as hydrobromic acid (HBr). Measurements made by Jay Park support the notion that the bromine is tied up as hydrobromic acid. However, there is evidence that these measurements are incorrect:

Watson indicated to me that Wes Traub used 2 different techniques and could not reproduce Park's results -- HBr was not measured.

In addition, Jim Anderson has made direct, in situ measurements at the poles and at midlatitudes. He has found significant concentrations of reactive bromine: In the midlatitudes: "BrO levels were 5 parts per trillion by volume between 18 and 21 kilometers, and 2.4 pptv below that altitude." Science (1988). Over Antarctica: 15 pptv. J.Geophys. Res. (1989). Over the Arctic: "Mixing rations of BrO have been measured in the arctic lower stratosphere...Observaitons from fourteen flights above the Arctc Circle...defined mixing ratios within the vortex of 4 +/- 2 pptv at a potential temperature of 400K, rising to 8 +/- 2 pptv at 470 K." Geophys. Res. Ltrs. (1990).

Substitutes

o Commodity Fumigant

M E M O R A N D U M

DATE: January 28, 1992

TO: Al

FROM: Katie

SUBJECT: Methyl Bromide meeting

****

Who will be here:

- o Bob Watson (NASA)
- o Susan Solomon (NOAA)
- o Eileen Claussen (EPA)
- o Steve Seidel (EPA)
- o Paul Bergson (an attorney who represents the methyl bromide industry on ozone issues)
- o Tom Duafala (*Trical Director of Research)
- o Harvey Shulman (*Trical lawyer)

*Trical does not produce methyl bromide; it formulates ag chemicals from CH3Br and retails.

Objective: The goal is to make a solid case that the production and use of methyl bromide (CH3Br) should be phased out in short order. Each of the participants in this discussion has received a copy of the draft bill (attached), and therefore knows that you propose to ban ch3br as of january 1, 1996.

Industry Arguments Against: In addition to the usual moaning and wailing, I anticipate the following: They will attack the sufficiency of our knowledge of the bromine budget -- what are the principle sources of atmospheric bromine?; even if CH3Br is a primary source of atmospheric bromine, does the CH3Br derive primarily from natural or anthropogenic sources; does CH3Br-derived bromine directly contribute to ozone loss -- i.e., does the CH3Br make it to the stratosphere to deliver its bromine payload, and if so, is the bromine found in active form (BrO) or is it held in a nonreactive sink (HBr)?; CH3Br is an essential agricultural product and we have no suitable substitutes.

NOTE THAT THEY MAY MENTION THAT THEY INTEND TO ESTABLISH A TWO MILLION RESEARCH EFFORT TO ENHANCE OUR UNDERSTANDING OF THE BROMINE BUDGET. DON'T BUY THIS. WE HAVE SUFFICIENT KNOWLEDGE OF THE BUDGET TO JUSTIFY ACTION

NOW, AND (AS I WILL DISCUSS FURTHER BELOW), THE OFFER IS A STALL TACTIC.

Bottom Line: It is true that we do not understand bromine chemistry as well as chlorine chemistry, however, we have evidence sufficient to counter the arguments relating to the bromine budget. The question of substitutes is a tougher one. For some of its uses, namely as a space and commodity fumigant, I have come across promising substitutes. For other uses, namely as a soil fumigant and fungicide and nematicide, the alternatives are not as apparant. However, on this score your message should be that industry should sink its 2 million not into further atmospheric chemistry research, but into finding safe substitute substances and/or processes.

Background on Methyl Bromide:

This sh*t is ubiquitous:

First introduced as an insecticide in 1932. Now used widely as a fumigant for all types of dry foodstuffs, especially produce contained in bags or packages ("commodity fumigant"). It is also used in mills, warehouses, ships, and frieght cars ("structural fumigant"); in greenhouses and fields for the control of nematodes, fungi, and weeds ("soil fumigant"). There are some 87 raw agricultural commodities on the list of foodstuffs that may legally be treated with ch3br, including 13 kinds of nuts, 10 kinds of grains, 36 kinds of vegetables, 19 kinds of fruits as well as every conceivable variety of processed foods. Moreover, USDA requires its use as a fumigant on a wide variety of imported fruits and vegetables as a condition of their entry into the US.

There also are non-ag uses, including industrial applications as a disinfectant, methylating agent and degreaser. Also used as a fire extinguisher (don't know if this use continues, as according to one article: "Originally, they used it in fire extinguishers, ... until they noticed certain people dropping dead whent they extinguished fires in closed spaces.")

SEE ATTACHED MAP OF USAGE IN THE UNITED STATES. NOTE THAT TENNESSEE IS A HEAVY USER. (Also note, curiously, that bread basket states do not rely on it).

This sh*t is nasty:

CH3Br is listed under the Toxic Chemical Release Inventory of the Community Right To Know Act as one of approximately 300 chemicals regarded as "acutely toxic, possible carcinogenic, or capable of having a significant

adverse effect on the environment." According to a 1990 Buzzworm article methyl bromide is "an extremely hazardous poison -- a poison with no known antidote, capable of causing symptoms ranging form headaches, vomiting and vertigo to psychosis, convulsions, delirium, respiratory failure and central nervous system depression resulting in death."

The most authoritative statement on the toxicology and carcinogenesis is Health and Human Service's 1990 National Toxicology Program report:

o it's toxic...."Short-term toxicity tests conducted in various species have shown that methyl bromide is highly toxic to mammals." Moreover, "serious exposure can occur without warning" because "methyl bromide has little odor at potentially toxic concentrations," and because methyl bromide is "extremely penetrating," "standard protective clothing did little to prevent exposure in fumigation operations".

o it's mutagenic...."exposure by inhalation of methyl bromide gas resulted in a significant increase in sex-linked lethal mutations in the germ cells" of male flies.

o it's lethal...."At least 115 known fatalities and 843 known systemic, skin, eye, and other injuries have resulted form methyl bromide exposure." (On this point see also Casarett and Doull's Toxicology: "methyl bromide is said to have been responsible for more deaths in recent years among occupationally exposed persons in California than all of the more publicized organophosphate group of insecticides").

o it's also controversial....

carcinogenic??

A Dutch government study startled EPA and NIH when it found that, in just 90 days, methyl bromide fed to rats produced cancerous tumors. NIH scientists subsequently reviewed the slides used in the Dutch study and concluded that the Dutch had misinterpreted them. According to the US researchers, what the rats developed were "hyperplastic lesions of the forestomach", not carcinoma. But, either way the news ain't good -- such "hyperplastic responses are usually characteristic of carcinogenic chemicals," and the lesions are often forerunners of carcinoma. Moreover, the Dutch suspect that the real reason US criticized their results was because EPA in 1983 had to place ethylene dibromide, a fumigant used for many of the same purposes as methyl bromide, under an emergency ban when it was discovered -- contrary to earlier EPA assurances -- to be a

strong carcinogen. I do not know what has been done since the Dutch study to resolve this question.

food residues??

Despite its acute toxicity and ubiquitous use, testing for ch3br residues in foodstuffs is not required (at least as of the writing of the Buzzworm article of March/April 1990). Why? Because, since it is used in gaseous form, it was assumed that none would persist to be absorbed by foodstuffs. The lid was blown on this idea, however, in the mid-1980's when, under a USDA quarantine program, methyl bromide residues were detected in California nuts and Florida citrus. And it is known that methyl bromide is very soluble in fats, so products containing high oil and fatty acid, such as nuts and cheese are likely to retain it. Nonetheless, the largest mfgrs of methyl bromide (Great Lakes Chemical Company and Ethyl Corp.) claim that they do test and have found no detectable levels of methyl bromide. Note here that, even if EPA decided to require such tests, it would be dependent on industry-submitted data.

Ozone Depletion:

From the recent 1991 UNEP/WMO International Ozone Trends Scientific Assessment:

"Stratospheric bromine is 30 - 120 times more efficient than stratospheric chlorine in destroying ozone on a per atom basis."

"Methyl bromide is the major contributor to stratospheric bromine (15pptv). The sources of methyl bromide are not well characterized; however, significant anthropogenic emissions have been suggested."

"If the anthropogenic sources of methyl bromide are significant and their emissions can be reduced, then each 10% reduction in methyl bromide would rapidly result in a decrease in strratospheric bromine of 1.5 pptv, which is equivalent to a reduction in stratospheric chlorine of 0.045 to 0.18 ppbv. This gain is comparable to that of a three-year acceleration of the scheduled phase-out of the CFCs.

Ozone Depletion Potential

Susan Solomon is a lead author of the chapter of the International Assessment dealing with ODPs. The best consensus is that the steady state ODP for ch3br is 0.6.

Susan emphasizes that this is a conservative value. "Steady states" values are determined on the basis of the amount of ozone depletion the substance in question would cause over a 100 year lifetime. CH3Br, however, is a very short-lived species -- 1-2 years. If instead we look at its ozone depletion potential over that time horizon, the extremely acute impact of ch3br on ozone becomes clear: "Note that although CH3Br displays a relatively small ODP over long time horizons, it has a very large ODP for short time scales by virtue of its short lifetime and the large value of [its ozone depletion efficiency relative to chlorine]." The implication is that controls on CH3Br will have significant, immediate impact on reducing the atmospheric concentration of ozone destructive substances.

Regulatory Implication and Your Legislation:

Pursuant to the Clean Air Act, EPA is required to list any substance with an ODP of 0.2 or greater as a Class I substance -- that is, as an ozone destroyer that will be completely phased out by 2000.

You must be careful to make clear to industry that you are not proposing new legislation because it is your opinion that EPA currently does not have authority to regulate ch3br and therefore new legislation is necessary. To the contrary, now that the ODP determination has been made, EPA does have that authority and in fact is required to act. The point of your legislation is not to establish EPA authority under Clean Air, but rather, to force EPA to go even further and faster than Clean Air permits.

What is the rationale for making EPA move faster??

First, the Parties to the Montreal Protocol in the next year will meet to decide on an accelerated phaseout schedule. Indications are that substances that would be considered "Class I" chemicals under Clean Air -- as ch3br now will be considered -- will be phased out by 1996 under the amendments that likely will be proposed. Therefore, you simply jump start the process and direct that that be the phaseout date for methylbromide. This is a favor to industry -- it's gonna happen anyway and you provide them with "regulatory certainty"....

Second, regardless of what occurrs internationally, the significant short term gains that can be had from ch3br regulation argue for an expedited process. If instead we wait for regulation pursuant to the current terms of the Clean Air Act, the process, involving public notice and hearings could be quite protracted.

Industry Response

Industry therefore knows there's trouble in paradise for them. (Meanwhile nematoids across the country are celebrating...). That does not mean however that they are prepared to raise the white flag. To the contrary, industry plans to fight the Clean Air Class I listing on the grounds that our knowledge of the bromine budget is insufficient, and consequently, the ch3br ODP determination is unsound. Also as indicated above, industry's game will be to propose a 2 million research effort to get a better handle on the chemistry (and to postpone immediate action).

Response to Industry Criticisms

o Is methyl bromide a significant source of atmospheric bromine?

As indicated above, the International Assessment states that methyl bromide is the major contributor to stratospheric bromine.

In addition, Anderson states in a 1989 article in Nature: Salawitch et al. "conclude that the total organic bromine source is between 6 and 20 pptv, with 3 pptv being the man-made perhalogenated bromine gases CF3Br and CF2BrCl, and the rest being methyl bromide".

o Even if methyl bromide is a significant source of atmospheric bromine, what proof is there that there is a significant anthropogenic contribution to atmospheric concentrations?

Industry will bolster this point by noting -- correctly -- that the oceans are a major natural source of CH3Br. In addition, industry also argues that its use of methyl bromide does not contribute to atmospheric concentrations because it gets degraded by soil microbes when it is injected into the ground. Taking each of these points in turn:

Ocean contribution:

Again, the international assessment said "significant anthropogenic emissions have been suggested." In addition, in a 1985 letter to Nature, Penkett et al. reported that "the weight of the evidence does not favor a large natural source [of ch3br. Rather], Our interpretation of the data ... suggests that the predominant source of CH3Br in the atmosphere is anthropogenic rather than natural."

I am unaware of any other natural terrestrial sources of CH3Br. And Grosjean reports in a 1991 article in J. Air Waste Manage. Assoc. that "There are no reactions by which methyl bromide may form in the atmosphere."

Soil Degradation:

Because CH3Br has C-H bonds, it is possible that bugs would eat it. I am unaware of any evidence demonstrating this, however.

Moreover, as noted above, direct injection into soil is only one of the uses of CH3Br. As indicated, there are significant non-agricultural uses. And even for the agricultural uses, methyl bromide is used as a space and commodity fumigant as well as a soil fumigant. When blasted into silos or on commodities, methyl bromide of course escapes into the atmosphere. Indeed it must be vented into the atmosphere because, since it is acutely toxic, humans could not enter premises where it has been used unless the premises had been fully aired. Venting is standard practice, and it has often been specifically because venting was not done thoroughly enough that humans have been killed -- sometimes instantly -- from exposure. Methyl bromide has a tendency to hide in "pockets" like bathrooms, drawers and other close spaces and therefore is not always fully flushed out in the venting process. Now that CH3Br is being used to fumigate homes and restaurants, etc. people have been killed when they encountered these lingering pockets.

o Even if anthropogenically-derived CH3Br is a major source of atmospheric bromine, how do we know that it makes it up to the stratosphere to deliver its bromine payload?

CALL CICERONE

To refer to Anderson's 1989 Nature article again, he cites Salawitch et al. for the proposition that 6-20 pptv of inorganic bromine is delivered to the "lower stratosphere" by organic gases, and primarily by CH3Br.

In addition, Grosjean states that: "Methyl bromide is one of the least reactive toxic air contiminants, with a correspondingly long persistence in the atmosphere. Reactions with O3 and NO3 are negligibly slow. Photolysis is a negligible removal process for CH3Br in the lower troposphere. Methyl bromide reacts only slowly with the hydroxyl radical." Therefore, ch3br survives the reactions that cleanse many other substances out of the troposphere. It therefore likely persists and makes its way into the stratosphere. As Grosjean continues: "Upward diffusion and

model calculations. Do in situ. US balloon did profiles but we stopped.

deposition are thus the dominant loss processes for CH3Br in the troposhere."

o Even if the bromine does get delivered to the stratosphere, does the bromine then destroy ozone?

The question here is whether the bromine in the stratosphere is in active form (BrO) or is trapped in a reservoir such as hydrobromic acid (HBr). Measurements made by Jay Park support the notion that the bromine is tied up as hydrobromic acid. However, there is evidence that these measurements are incorrect:

Watson indicated to me that Wes Traub used 2 different techniques and could not reproduce Park's results -- HBr was not measured.

In addition, Jim Anderson has made direct, in situ measurements at the poles and at midlatitudes. He has found significant concentrations of reactive bromine: In the midlatitudes: "BrO levels were 5 parts per trillion by volume between 18 and 21 kilometers, and 2.4 pptv below that altitude." Science (1988). Over Antarctica: 15 pptv. J.Geophys. Res. (1989). Over the Arctic: "Mixing rations of BrO have been measured in the arctic lower stratosphere...Observaitons from fourteen flights above the Arctc Circle...defined mixing ratios within the vortex of 4 +/- 2 pptv at a potential temperature of 400K, rising to 8 +/- 2 pptv at 470 K." Geophys. Res. Ltrs. (1990).

Substitutes

o Commodity and Structural Fumigant:

--chemical alternative is PHOSPHINE: ADVANTAGE of phosphine is that it does not leave residues on food; DISADVANTAGE is that it is toxic and so safety precautions necessary during fumigation.

--promising non-chemical alternative is a CONTROLLED ATMOSPHERE PROCESS:
Controlled atmosphere disinfestationl of stored products works by asphyxiating stored product pests. The controlled atmospheres for insect disinfestation usually involve reducing the oxygen concentration to less than 1 percent and/or increasing the carbon dioxide to well above 10 percent. ADVANTAGE is that the process leaves no potentially toxic residues on the product; they are nonpolluting; and they are safer to apply cause they do not involve handling of toxic substances. The process has also been shown to be effective in maintaining product quality as

long as the controlled atmosphere conditions are continued during storage. In addition, one method of controlled atmosphere generation -- use of on-site low oxygen atmosphere generators, is competitive with chemical disinfestation. (Also -- could this possibly be a commercially valuable use of CO2 sequestered from coal????) DISADVANTAGE is that longer exposure times are required for controlled atmosphere treatments than for chemical treatments. There is also a potential risk of increased tolerance over time to low oxygen and/or high carbon dioxide concentrations by stored product pests -- altho this reisk is considered to be less significant than it is in the case of chemical treatments.

o Soil Fumigant

--chemical alternatives include TELONE (disadvantage is that it is a less effective herbicide, and its registration has been removed in some areas); DAZOMET (disadvantage is that it is not registered for food crops); METHAM-SODIUM (disadvantage is that it requires drip irrigation system); VORLEX (disadvantage is requires long waiting period before planting).

**Note there may be other alternatives -- this is from a very preliminary list compiled by EPA.

-- Biotech

deposition are thus the dominant loss processes for CH3Br in the troposhere."

o Even if the bromine does get delivered to the stratosphere, does the bromine then destroy ozone?

The question here is whether the bromine in the stratosphere is in active form (BrO) or is trapped in a reservoir such as hydrobromic acid (HBr). Measurements made by Jay Park support the notion that the bromine is tied up as hydrobromic acid. However, there is evidence that these measurements are incorrect:

Watson indicated to me that Wes Traub used 2 different techniques and could not reproduce Park's results -- HBr was not measured.

In addition, Jim Anderson has made direct, in situ measurements at the poles and at midlatitudes. He has found significant concentrations of reactive bromine: In the midlatitudes: "BrO levels were 5 parts per trillion by volume between 18 and 21 kilometers, and 2.4 pptv below that altitude." Science (1988). Over Antarctica: 15 pptv. J.Geophys. Res. (1989). Over the Arctic: "Mixing rations of BrO have been measured in the arctic lower stratosphere...Observaitons from fourteen flights above the Arctc Circle...defined mixing ratios within the vortex of 4 +/- 2 pptv at a potential temperature of 400K, rising to 8 +/- 2 pptv at 470 K." Geophys. Res. Ltrs. (1990).

Substitutes

o Commodity and Structural Fumigant:

--chemical alternative is PHOSPHINE: ADVANTAGE of phosphine is that it does not leave residues on food; DISADVANTAGE is that it is toxic and so safety precautions necessary during fumigation.

--promising non-chemical alternative is a CONTROLLED ATMOSPHERE PROCESS:
Controlled atmosphere disinfestationl of stored products works by asphyxiating stored product pests. The controlled atmospheres for insect disinfestation usually involve reducing the oxygen concentration to less than 1 percent and/or increasing the carbon dioxide to well above 10 percent. ADVANTAGE is that the process leaves no potentially toxic residues on the product; they are nonpolluting; and they are safer to apply cause they do not involve handling of toxic substances. The process has also been shown to be effective in maintaining product quality as

long as the controlled atmosphere conditions are continued during storage. In addition, one method of controlled atmosphere generation -- use of on-site low oxygen atmosphere generators, is competitive with chemical disinfestation. (Also -- could this possibly be a commercially valuable use of CO2 sequestered from coal????) DISADVANTAGE is that longer exposure times are required for controlled atmosphere treatments than for chemical treatments. There is also a potential risk of increased tolerance over time to low oxygen and/or high carbon dioxide concentrations by stored product pests -- altho this reisk is considered to be less significant than it is in the case of chemical treatments.

o Soil Fumigant

--chemical alternatives include TELONE (disadvantage is that it is a less effective herbicide, and its registration has been removed in some areas); DAZOMET (disadvantage is that it is not registered for food crops); METHAM-SODIUM (disadvantage is that it requires drip irrigation system); VORLEX (disadvantage is requires long waiting period before planting).

**Note there may be other alternatives -- this is from a very preliminary list compiled by EPA.

--other options include possible developments in BIOTECHNOLOGY -- genetic alteration of crops to resist soil dwelling microbes and CROP ROTATION naturally to resist pests.

General commentary on Substitutes: Some companies -- notably, the PLANTERS COMPANY, PILLSBURY, AND KELLOGGS prohibit its use on any of its food products, so there must be other ways to protect food. Also, the map EPA has provided shows that ch3br is not used in the midwest -- therefore there must be alternatives for the corn, wheat, soybean, etc. that is grown there.

Some Considerations Regarding Methyl Bromide (CH_3Br)

Susan Solomon and Dan Albritton
NOAA Aeronomy Laboratory

1) The role of CH_3Br in ozone loss. Observations have demonstrated that bromine is very effective at destroying stratospheric ozone as compared to chlorine. In the Antarctic, two independent sets of measurements show that bromine is about 40 times more effective than chlorine for ozone destruction. Similar numbers are also true for the Arctic. The extreme efficiency of bromine for ozone destruction is related to a reaction involving chlorine monoxide and bromine monoxide, so that chlorine and bromine chemistries are coupled. Thus, this extreme potency is related to the elevated levels of chlorine in today's atmosphere (about 3.5 ppbv compared to natural levels of only 0.6 ppbv) and will prevail as long as chlorine remains elevated (e.g., the next 50-100 years).

2) The sources/sinks of CH_3Br. The abundance of CH_3Br in today's atmosphere is about 7-15 parts per trillion by volume (pptv), and its atmospheric lifetime is roughly 1-2 years. Based on these numbers and assuming approximate balance between production and loss (since the lifetime is rather short), the global production of CH_3Br from both natural and manmade sources must be on the order of 100-500 million kg/year. The sink for CH_3Br is mainly reaction with OH. Hydrochlorofluorocarbons (HCFCs) have the same sink mechanism, so the uncertainty in the CH_3Br sink and lifetime is the same as that for the HCFCs.

if we regulate HCFC's, so - no greater uncertainty here.

U. S. production is estimated to be 50 million pounds/year, or about 20 million kg/year. This is between 4 and 20% of the above numbers. For the CFC's, ~~global~~ U.S. production is about 35-50% of the total global production (depending upon the specific CFC in question). If CH_3Br is similar, then as much as 8-40% of the global prodcution may be manmade.

Q: How much is global production (U. S. and non-U.S.)?

10

3) *Production versus release of CH_3Br to the atmosphere.* Because the major use of CH_3Br is as a fumigant in agricultural applications, the question of how much gets to the atmosphere must be considered. It is possible that some or even all of the CH_3Br is taken up by the soil and microbes therein during application. In this case the release of CH_3Br to the atmosphere would be less than its production. This is a major unknown.

Q: Are there any scientific studies of soil uptake?

4) *The impact of a CH_3Br reduction on the ozone layer.*

From UNEP/WMO (1992):

If indeed as much as 8-40% of the release of CH_3Br is man-made, then it is possible to lower stratospheric CH_3Br abundances by reducing these emissions. A 10% reduction in methyl bromide emissions would rapidly decrease stratospheric bromine by 0.7-1.5 pptv. Since the lifetime of CH_3Br is only a few years, the change would occur rapidly after cessation of emissions. Such a gain would be comparable to a 3-year acceleration of the phaseout of CFCs.

5) *The ODP of CH_3Br, and its relationship to natural sources.*

Each molecule of CH_3Br emitted to the atmosphere has a certain impact on the ozone layer over a specific time horizon.

The steady state ODP of CH_3Br is about 0.6. This describes the impact of release of a kilogram of CH_3Br on the ozone layer over time scales of the order of 100 years, compared to release of the same amount of CFC-11. Like other short-lived molecules, its short-term ODP is far greater. The CH_3Br ODP over the 5-10 year time horizons is about 5-15. Over the next ten to twenty years, total chlorine and bromine levels will attain the highest values ever experienced on the planet Earth. During this key period, CH_3Br has the highest ODP of currently uncontrolled substances.

Whether or not the manmade emission of CH_3Br is larger than the natural sources is not relevant to these numbers: they reflect the impact of each molecule emitted. It is sometimes argued that emissions don't matter as long as the amount of substance accumulated in the atmosphere is small, or is less than that which is natural. This argument is wrong because each molecule emitted, no matter what its origin, has an impact on the ozone layer. To carry this point to an extreme, assume that there were 1000 different possible substitutes for CFC-11. By using them all in small amounts, none would ever attain atmospheric levels comparable to CFC-11, but each would contribute to ozone loss according to the number of molecules released. Thus the ODP is the proper way to describe the relative impact of any manmade emission upon the ozone layer regardless of atmospheric abundances.

12

Aeronomy Laboratory

Aeronomy Laboratory/ERL/NOAA
325 S. Broadway, R/E/AL
Boulder, Colorado 80303

FROM: Dr. Susan Solomon
TEL: (303) 497-3483; FTS 320-3483
FAX: (303) 497-5373; FTS 320-5373

TO: Katie McGinty
Tel: 202-224-4944
Fax: 202-224-0580
DATE: January 26, 1992 **Page 1 of 4**

Dear Katie,

The attached write-up summarizes some thoughts Dan Albritton and I have had regarding methyl bromide.

I'll be leaving Boulder at about 1:00 pm on Monday. I'm staying at the River Inn in Washington, and can be reached there on Monday night or Tuesday morning. Unless I hear differently from you, I'll look forward to meeting you at 12:30 on Tuesday at Senator Gore's office in the Russell Senate Office Building. Please let me know if there is any change in scheduling, etc., or if you have any questions I can help with.

Best wishes,

Susan S.

Table 7. Distribution of Methyl Bromide Consumption in the U.S., 1988

Use Area	Percent of Total
Soil Fumigant	55
Space and Structure Fumigant	10
Chemical Processes	10
Grain and Commodity Fumigant	5
Exports	20

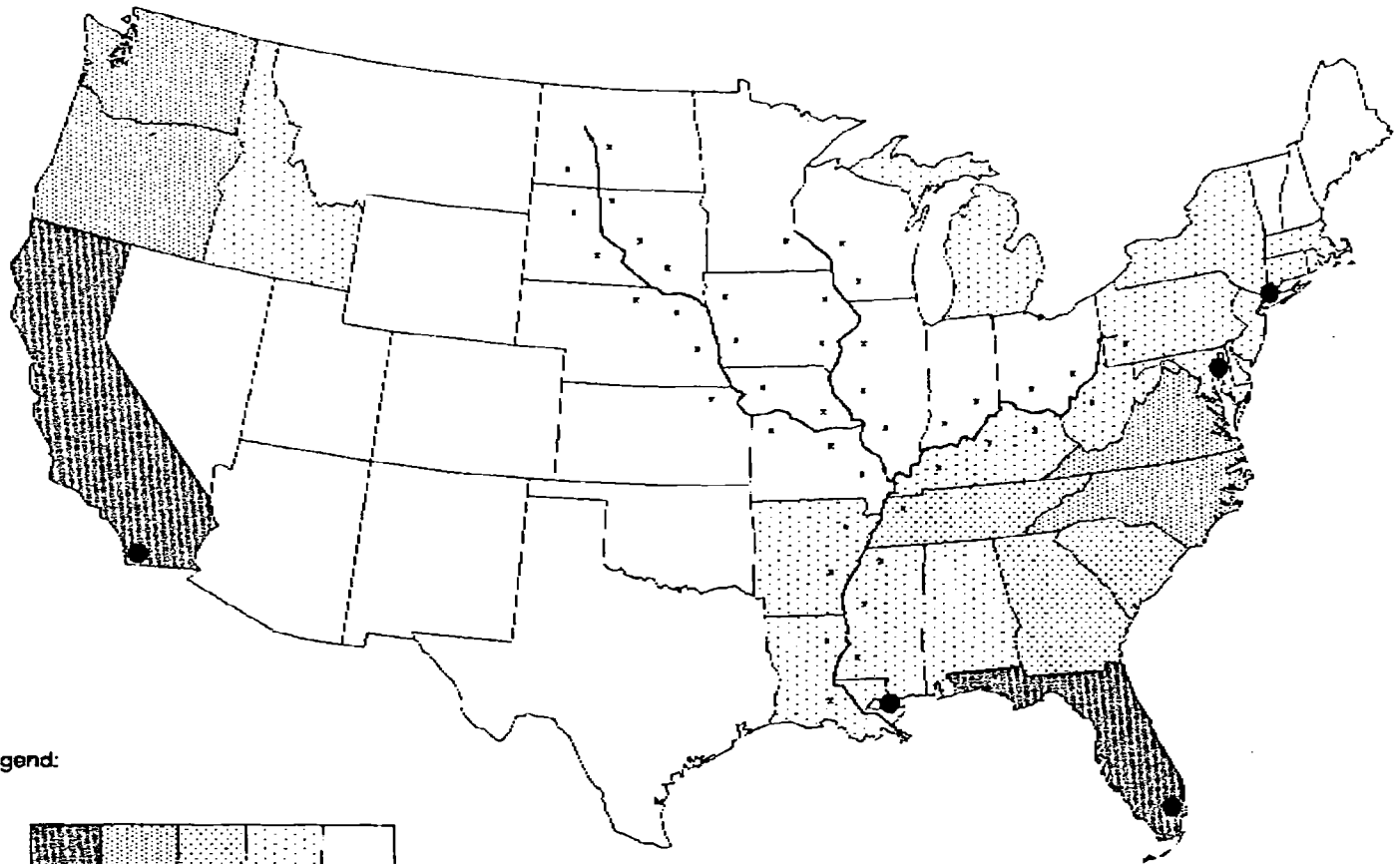
Source: CMR 1988a.

Table 8. Uses of Methyl Bromide

Use Area	Crops
Soil fumigant	asparagus, broccoli, cauliflower, eggplant, lettuce, melons, peppers, pineapple, tobacco, and others
Fungicide and nematicide	fruit tree and vineyard sites, plantbeds, tomatoes, strawberries, and others
Commodity fumigation	barley, beans, beets, cabbage, carrots, chestnuts, citrus, lemons, figs, oats, rice, rye, peanuts, spices, apricots, pecans, pumpkins, dates, agricultural premises, and others
Space fumigation	warehouses, trucks, railroad cars, food processing plants, barns, feed rooms, grain bins, greenhouses, poultry houses, bags, boxes, crates, and other areas

Source: Thomson 1991.

Figure 1. U.S. Use Pattern for Methyl Bromide



? = grain belt
- not used for corn, wheat, soybean ??

POTENTIAL METHYL BROMIDE SUBSTITUTES
SOIL FUMIGANTS

Pesticide	Disadvantages
Telone	Less effective as herbicide; registration removed in some areas
Dazomet	Not registered for food crops
Metham-sodium	Requires drip irrigation system
Vorlex	Long waiting period before planting

Table 6-5. Range of Modelled and Semi-Empirical Steady-State ODPs and Recommended Best Estimates

Species	Model Range		Semi-Empirical Range		Best
	ODP	ODP/CLP or ODP/BLP	ODP	ODP/CLP or ODP/BLP	Estimate ODP
CFCs					
CFC-11	1.0	1.0	1.0	1.0	1.0
CFC-12	0.88 - 1.06	0.551 - 0.665			≈1.0
CFC-113	0.92 - 1.01	0.631 - 0.690	1.07	0.75	1.07
CFC-114	0.57 - 0.82	0.266 - 0.382			≈0.8
CFC-115	0.29 - 0.48	0.099 - 0.161			≈0.5
HCFCS, etc.					
HCFC-22	0.032 - 0.048	0.221 - 0.314	0.05-0.08	0.33-0.55	0.055
HCFC-123	0.013 - 0.020	0.709 - 1.050	0.02	1.112	0.02
HCFC-124	0.016 - 0.034	0.358 - 0.793	0.022	0.523	0.022
HCFC-141b	0.10 - 0.12	0.650 - 0.767	0.11	0.70-0.72	0.11
HCFC-142b	0.035 - 0.057	0.186 - 0.305	0.06-0.07	0.33-0.39	0.065
HCFC-225ca	0.016 - 0.020	0.714 - 0.920	0.025	1.093	0.025
HCFC-225cb	0.023 - 0.031	0.348 - 0.474	0.033	0.50	0.033
CCl_4	1.03 - 1.15	1.014 - 1.130	1.05-1.11	1.03-1.09	1.08
CH_3CCl_3	0.11 - 0.13	0.968 - 1.130	0.122-0.124	1.07-1.09	0.12
Brominated Compounds					
H-1301	10.0 - 12.7	23.9-32.2	15.2-17.2	40	≈16
H-1211	1.8 - 5.0	16.3-49.6	3.9-4.4	40	≈4
H-1202	1.7	52.9	1.25	40	≈1.25
H-2402	6.4 - 10.2	42.1-47.8	5.9-8.5	40	≈7
H-1201	1.4	35.1	1.4	40	≈1.4
H-2401	0.4	66.4	0.25	40	≈0.25
H-2311	0.3	79.9	0.14	40	≈0.14
CH_3Br	0.5-0.7	30.6-67.7	0.44-0.69	40	≈0.6

Table 6-3. Derived ODPs scaled to UNEP standardized lifetimes and the model-derived ODP/CLP ratio from the two-dimensional models for each of the compounds examined. Based on gas-phase chemistry only results unless indicated otherwise. Brackets indicate derived values with heterogeneous chemistry in the model. For all halons, model-derived ODPs are presented without reference to the standardized lifetime.

Species	LLNL		AER		OSLO		Du Pont	
	ODP	ODP/CLP or ODP/BLP	ODP	ODP/CLP or ODP/BLP	ODP	ODP/CLP	ODP	ODP/CLP
<u>CFCs</u>								
CFC-11	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CFC-12	0.88	0.551	0.93	0.586	0.95 [0.93]	0.595 [0.582]	1.06 [1.01]	0.665 [0.635]
CFC-113	0.92	0.631	1.01	0.690	0.99 [0.98]	0.675 [0.668]		
CFC-114	0.57	0.266	0.82	0.382				
CFC-115	0.29	0.099	0.48	0.161				
<u>HCFCS, etc.</u>								
HCFC-22	0.034	0.221 [0.231]	0.045 [0.039]	0.276 [0.255]	0.032 [0.082]	0.221	0.048 [0.043]	0.314 [0.286]
HCFC-123	0.019 [0.016]	0.944 [0.878]	0.020	1.05			[0.013]	[0.709]
HCFC-124	0.016	0.358	0.020	0.449			[0.034]	[0.793]
HCFC-141b	0.12 [0.11]	0.720 [0.731]	0.12	0.767			[0.105]	[0.650]
HCFC-142b	0.035 [0.037]	0.186 [0.200]	0.057	0.305			[0.054]	[0.289]
HCFC-225ca	0.020	0.856	0.021	0.920			[0.016]	[0.714]
HCFC-225cb	0.023	0.348	0.031	0.474			[0.024]	[0.370]
CCl_4	1.03	1.014	1.15 [1.13]	1.13 [1.11]				
CH_3CCl_3	0.11 [0.13]	0.968 [1.12]	0.13	1.13			0.12 [0.12]	1.032 [1.08]
<u>Halons, etc.</u>								
H-1301	12.7	32.2	10.03	23.9				
H-1211	5.0	49.6	1.8	16.3				
H-1202	1.7	52.9						
H-2402	6.4	42.1	10.2	47.8				
H-1201	1.4	35.1						
H-2401	0.44	66.4						
H-2311	0.28	79.9						
CH_3Br	0.74	67.7	0.62 [0.53]	35.8[30.6]				

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Atmospheric & Indoor Air Programs (OAIAP)
Washington, DC 20460

EPA

FACSIMILE COVER SHEET

⇒ ⇒ ⇒ ⇒ *Please Print in Black Ink Only* ⇐ ⇐ ⇐ ⇐

TO KATY MCGINTY	TELEPHONE #
OFFICE OF AL GORE	FAX PHONE # 224-0560
FROM DANIEL BLANK	TELEPHONE # 260-6628

INFORMATION FOR SENDING FACSIMILE MESSAGES

OFFICE	MAIL CODE	LOCATION	FACSIMILE TELEPHONE NUMBERS FTS	FACSIMILE TELEPHONE NUMBERS COMMERCIAL	VERIFICATION TELEPHONE NUMBERS FTS	VERIFICATION TELEPHONE NUMBERS COMMERCIAL
OAQPS - WO	ANR 443	Rm 933 WT	260-0451	(202) 260-0451	260-5575	(202) 260-5575
OPAR	ANR 443	Rm 925 WT	260-9766	(202) 260-9766	260-5580	(202) 260-5580
OPMO	ANR 455	RM 947 WT	260-4185	(202) 260-4185	260-7415	(202) 260-7415
OMS	ANR 443	RM 901 WT	260-3730	(202) 260-3730	260-7645	(202) 260-7645
IO	ANR 341W	RM 937 WT	260-7165	(202) 260-7155	260-7400	(202) 260-7400
SSCD	EN 341W	8th Floor Crystal Mall	398-8739	(703) 398-8739	308-8600	(703) 308-8600
OAIAP	ANR 443	Rm 735 WT	260-7991	(202) 260-7991	260-7407	(202) 260-7407
ORP	ANR 445	RM 201 NE	260-8347	(202) 260-8347	260-9600	(202) 260-9600

Comments BACKGROUND INFO ON METHYL BROMIDE.
LOOKING FORWARD TO OUR MEETING
TUESDAY.

PAGE 1 OF 7 PAGES (INCLUDING COVER SHEET)

METHYL BROMIDE

PURPOSE: To provide for the phase-out of production and consumption of methyl bromide.

FINDINGS: The Congress finds the following:

The stratospheric ozone layer which protects all living things from harmful ultraviolet radiation from the sun has been significantly depleted in nearly all areas of the globe due to the action of halogenated chemicals.

Recently, the United Nations/World Meteorological Organization International Ozone Trends Scientific Assessment Panel reported that the depletion is occuring twice as rapidly as had previously been measured or predicted; is persisting into the warmer months of the year, and has reached significant levels even in summer.

These findings necessitate a reappraisal of both domestic and international policy on the control of ozone destroying chemicals.

Stratospheric bromine is 30 - 120 times more efficient than stratospheric chlorine in destroying ozone on a per atom basis and the major source of stratospheric bromine is methyl bromide.

Methyl bromide is not currently regulated under the Clean Air Act amendment of 1990.

Reductions in emissions of methyl bromide would contribute effectively to the restoration of the ozone layer.

PHASE-OUT: Effective January 1, 1996, it shall be unlawful for any person to produce or consume, or import for consumption, methyl bromide in the United States, except where such person can be demonstrated that any such production or consumption does not result in destruction of the stratospheric ozone layer.

ECOSCIENCE

DANGEROUS LIAISONS

The Alarming Disclosure Of Methyl Bromide

BY LINDA AND BILL BONVIE

When viewed for the first time, the neighborhood might appear to be just another of those faded residential/industrial enclaves so characteristic of New England mill towns. Upon entering Carter Street, a narrow, shady thoroughfare whose timeworn frame houses are brightened by an occasional splash of flowers or trellised rosebush, your initial impression is apt to be of kids riding bikes. Go a bit further, and just beyond the old-fashioned Cardinal O'Connell Elementary School, you'll find yourself looking up at what the trees had partially obscured—the ivy-blanketed facade of a four-story brick factory building.

Welcome to Spaghettiville, U.S.A. Here, just outside downtown Lowell, Massachusetts, many of the pasta products made by the Prince Company, a Borden subsidiary (including some of those sold under the Creamettes label and various private ones) are processed and packaged for the journey that will end at countless American dinner tables.

Not only are the products turned out here of a benign and pleasurable variety, but adjacent to the factory has been created a kind of urban mini-oasis featuring an old-world style restaurant (the Prince Grotto) and outdoor terrace, along with gardens and a museum. Resplendent with Italian statuary and aesthetic touches, it's a natural setting for wedding receptions as well as a popular local tourist attraction—except on two particular weekends each year. At these times in the spring and fall, normal operations are suspended while the entire facility is sealed off and the perimeters of the property are posted with security guards whose job it is to bar everyone from entering. Everyone, that is, but certain specially licensed individuals equipped with protective gear, self-contained breathing apparatus and pressurized steel cylinders.

Encapsulated in these cylinders is a frigid liquid which, when heated, will emerge in the form of a gas—an invisible, odorless and highly lethal one. Over the course of a 24-hour period more than 9,000 pounds of this poison gas will penetrate every nook and cranny of the building, along with the packaged foods it contains—circulated by fans in order to counteract a tendency to sink at room temperatures. Then, within a short time of having accomplished its purpose—the eradication of any bugs that might have been on the premises—the gas will be vented out of the plant and into the environment shared by the homes, stores and classrooms of Spaghettiville, U.S.A.

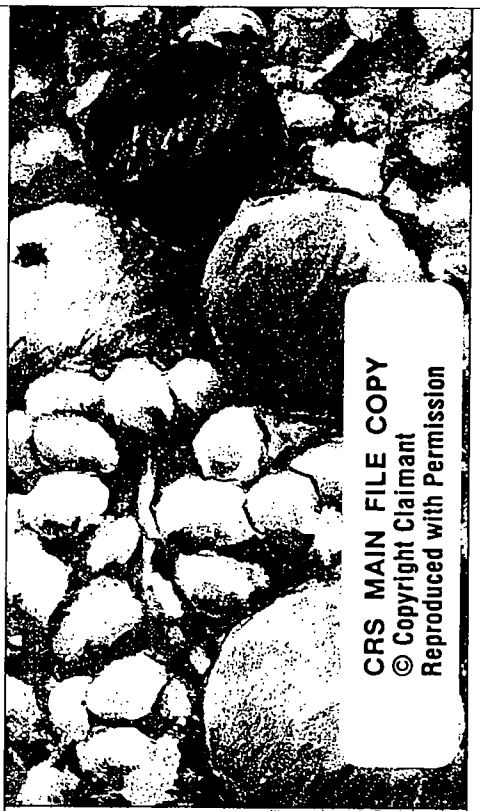


Illustration: Jill Englebardt

Like all large-scale offensive operations, the war on bugs and other pests is one that relies heavily on secrecy. In this case, however, the purpose is not to withhold information from an enemy, but rather to keep the public as uninformed as possible regarding the nature of the chemical weapons involved. The less the general populace knows about them, the more apt it is to assume that the government is doing an adequate job of preventing "civilian casualties" from becoming a by-product of that war.

Increasingly in recent months and years, however, that assumption has been called into question, and the appearance of responsible regulation has had to be reinforced by some type of action. This has sometimes resulted in a substance being deemed expendable—one of the latest examples being that of Alar, removed from circulation only after "60 Minutes" focused national attention on its residues and their carcinogenic potential, which had been of concern to environmentalists for years. And Alar, it should be noted, wasn't even an actual pesticide—merely a ripening agent used to help keep red apples on trees and make them more appealing to consumers.

When the Federal Food and Drug Administration ordered that millions of dollars worth of produce arriving from Chile be kept off supermarket shelves last winter, it appeared to be another indication of the lengths to which the U.S. government was willing to go to protect consumers. Even though the discovery of cyanide that prompted this seemingly drastic action involved only miniscule amounts—said to be relatively harmless—in exactly two grapes, no chances would be taken. With the notoriety attached to cyanide, it didn't call for a degree in chemistry to know that the grapes had somehow come into contact with a dangerous killer.

The name "methyl bromide," by contrast, has no such widespread recognition attached to it. Familiar mostly to exterminators, chemists, toxicologists and coroners, it, too, signifies an extremely hazardous poison—a poison with no known antidote, capable of causing symptoms ranging from headaches, vomiting and vertigo to psychosis, convulsions, delirium, respiratory failure and central nervous system depression resulting in death. It is also one to which *all* imported Chilean grapes, peaches, plums, apricots, nectarines and other agricultural commodities are routinely and deliberately exposed—something the federal government is well aware of, but so far has made no move to curtail. In fact, it's a direct result of standing orders from an agency of the federal government itself.

As the Department of Agriculture's current "chemical of choice" to keep the country free of alien insect life forms, methyl bromide—or bromomethane, as it is generically referred to—has been mandated for use as a fumigant on a virtual cornucopia of imported fruits and vegetables as a condition of their entry into the U.S. It is also registered for a variety of soil, postharvest and structural applications by virtue of its effectiveness at killing bugs, its unusual penetrating power, nonflammability and presumed rapid dissipation when aerated.

March/April 1990, v. 2, p. 40-45

One measure of just how pervasive methyl bromide's use has become is the list of foodstuffs that may be legally treated with it. There are 87 raw agricultural commodities on the list, including 13 kinds of nuts, 10 kinds of grains, 36 kinds of vegetables (from beans to yams) and 19 kinds of fruit, as well as every conceivable variety of processed foods.

Another indicator can be found in the Toxic Chemical Release Inventory of the 1986 Emergency Planning and Community Right to Know Act. Under the Bhopal-inspired legislation, the compound is listed as one of approximately 300 chemicals regarded as "acutely toxic (that is, causing serious injuries with short-time exposures), possible carcinogenic, or capable of having a significant adverse effect on the environment." According to the latest data put out at the beginning of 1990, some 1,178,517 pounds of this odorless, colorless gas--3.3 times as heavy as air--were released into the environment during 1988 by various reporting facilities within U.S., mostly in the form of stack and fugutive air emissions. Among those operations emitting the chemical were the Gerber Baby Food plant in Fort Smith, Ark. (22,660 pounds), the Hershey Chocolate plant in Hershey, Pa. (40,591 pounds), the H.B. Reese Candy Co., also in Hershey, Pa. (13,400 pounds), three Nabisco plants in Chicago, Atlanta and Niagara Falls (38,500 pounds combined), two Borden company facilities in Warren, Mich., and Lowell, Mass. (32,586 pounds combined), the Quaker Oats plant in Kankakee, Ill. (33,000 pounds) and a Quaker Oats subsidiary, Golden Grain Company, makers of Rice-A-Roni and Noodle-Roni products (14,000 pounds). These figures exclude any uses that may have fallen below the official reporting threshold.

The question of whether such massive releases represent a health hazard to nearby residents is one that still appears to be awaiting some sort of official answer. However, when put to Dr. David Groth, a Cincinnati-based consultant in occupational and environmental health and 24-year veteran of the National Institute of Occupational Safety and Health (NIOSH), he replied: "It's reasonable to expect if nobody is allowed in the building and venting takes place soon after fumigation, the gas is not going to decompose that rapidly, so any people who are downwind from the exhaust would be affected." Groth estimated that under such circumstances, "probably 90%" of the gas used in fumigation would actually end up being emitted into the environment.

During his career as a homicide detective with Miami's Metro Dade Police Department, Archie Moore has become well inured to all manner of untimely, crime-related deaths. But he still hasn't forgotten a particular one he investigated four years ago. It occurred at the end of October, following a burglary at what he describes as a "very nice home" in the city's southwest section.

"This guy took it upon himself to break into a house that had an enormous tent on it," Moore recalls. "Apparently, he wasn't in there very long (when) I guess the fumes and stuff started to overcome him. When we found him, he had collapsed in the back yard a few feet from the house."

For Danilo Leon Zuaznabar, a Venezuelan immigrant and petty criminal, this was the one offense for which there would be no chance of rehabilitation. To police who were summoned to the scene around midnight, however, this was not immediately evident, as Zuaznabar sat up when they arrived, appearing "groggy but coherent," according to their report. Then, having been read his rights in both English and Spanish, he voluntarily told the officers, "I broke into the house—I'm gassed." Still, his condition did not seem to warrant the services of a fire/rescue unit that had also responded. Instead, he was transported by police car to a special ward of Jackson Memorial Hospital reserved for offenders. After walking only five or six feet from the vehicle, however, Zuaznabar "collapsed on the ground and began experiencing what appeared to be convulsions,"

The EPA's official position is to continue to allow all currently registered products containing the poison to be "sold, distributed, formulated and used."

whereupon he was transferred to the emergency room. About ten and a half hours after being discovered on the lawn, he expired—the cause of the death being listed by the Medical Examiner's office as methyl bromide intoxication.

In the view of Dr. Thomas V. Briggle, the Zuaznabar case isn't all that unusual, but rather "follows a pattern" of similar episodes during tent fumigation in the state of Florida. Typically, says the University of Miami epidemiology and public health professor, "you'll find the perpetrator lying on the front lawn convulsing." And "they're not in (the house) for ten minutes."

But "considering the fact that methyl bromide is absorbed through the skin as well as inhaled, you get quite an exposure going into a tented home," he contends. "I mean, these things are robbed by people with breathing apparatus . . . and they die . . . it gets them either way."

Briggle, who is currently conducting a study in conjunction with the Occupational Safety and Health Administration (OSHA) on applicator-related hazards of methyl bromide, says he attempted a few years ago to develop a viable test for exposure to the chemical, using the bodies of such victims. The effort, however, was unsuccessful, due to the fact that the chemical "is altered so rapidly in the body" and breaks down in the bloodstream after only a very short period. The conventional test for blood bromide levels really "doesn't tell you anything," he claims, because these can be related to so many factors, from bromides in drinking water to antacids.

Relatively high concentrations, Palm Beach Medical Examiner Dr. John V. Marraccini says, can cause victims to undergo seizures or exhibit flu-like symptoms, then "Quickly develop lung failure." He cites an example of a 27-year-old woman who died some years ago after the gas leaked into her apartment from an adjoining building via a wall opening. "At 1 A.M., she was seen by a visiting doctor because she had abdominal cramps, vomiting, weakness. He decided she had the flu. She died in her bed about two and a half hours later." Then, there are the "more insidious" effects of chronic exposure to lesser amounts—the kind Marraccini claims are sometimes found among California agricultural industry workers. These may not only resemble liver disease or Reyes Syndrome, but can also include "a variety of neurological problems and psychiatric disorders"—some of them permanent. In other words, "chronic low-level exposure can make you look like you're nuts."

Marraccini also has a word of caution for homeowners about certain aspects of the gas that may elude those whose job it is to test atmospheric levels after a fumigated house has been vented. While a reading of five parts per million supposedly indicates it's safe to reenter, he points out that the vapors have a tendency to lurk in "pockets" (this hide-and-seek characteristic was alluded to at a recent technical seminar by a fumigation supply firm service manager who noted that "we may not get any gas in a room, but the drawers or closets may be full of methyl bromide"). There's also the hidden danger of methyl bromide getting into air spaces of foam material that's been left in an area undergoing fumigation. "You could put a child down on a mattress and expose him to methyl bromide leaking out of the air cells. That potential exists."

Marraccini contends that cases of methyl bromide poisoning really began "burgeoning" in his jurisdiction around 1981. Its pernicious tendencies, though, were noted many years before when it played a somewhat different role in protecting structures. "Originally, they used it in fire extinguishers," he says, and they noticed certain people dropping dead when they extinguished fires in closed spaces." So it proved less than ideal in this capacity.

"But it did kill bugs."

Whether methyl bromide should be permitted to go on killing bugs is a question that the Environmental Protection Agency is currently in the process of reviewing. As a compound up for rereg-

istration, the safety of its various long-accepted and officially sanctioned uses must now supposedly be proven to the agency's satisfaction.

"If you have an old chemical like methyl bromide . . . and you were to look at it under the same kind of magnifying glass that you use in registering new compounds, it wouldn't pass muster," says one EPA researcher. "There are a lot of questions which we don't know the answer to. One . . . is whether or not you have any residues (in food) because it's a gas—won't it go away? Well, that was always the assumption . . . and no one had gotten the residue data to see how much persisted. After all, that was the assumption with EDB also, and it wasn't true."

EDB—ethylene dibromide—was the fumigant placed under an emergency ban by the EPA in 1983 after it was deemed a strong carcinogen and its presence was detected in various foods and groundwater. Also an organic halide, EDB was, up until then, used for many of the same purposes that methyl bromide currently is—including the gassing of imported commodities. In a report issued the year after the ban, however, the American Council on Science and Health, which opposed the action, termed methyl bromide as "more poisonous" and posing a greater hazard to the safety of exposed workers than EDB.

Those exposed workers are a prime concern of at least one organization, Cesar Chavez' United Farm Workers of America. Methyl bromide's application to the soil beneath vineyards, according to Chavez, had caused a number of them to be poisoned—sometimes long after fumigation. As a result, an industry ban on the chemical's use is one of the stated purposes of the UFW's current grape boycott.

The EPA's own findings lend credence to this position. In California, it ranked the compound as one of the major causes of poisonings and hospitalizations of workers from 1982-85.

In a number of cases, people residing in the vicinity of fumigated agricultural land appear to also have suffered various ill effects. One such well-documented episode involved the evacuation of about 75 homes near Modesto in 1984 following the soil treatment of a strawberry field with methyl bromide and chloropicrin, another fumigant with its own irritating side effects (resembling those of tear gas) sometimes added in small amounts to give off a "warning odor." The incident resulted in some 35 individuals having to be treated at local hospitals, including several police officers and fire fighters called in to assist and a six-year-old child who was hallucinating.

It was around the mid-1980s, under a USDA quarantine program, that methyl bromide residues were first detected in California nuts and Florida citrus, according to Walter Francis, contact person for the Pesticide Management Team in the EPA's Registration Division. "We started getting information that organic methyl bromide was indeed being found. . . . I think we were under the impression at one point that it wasn't there."

That "impression" was one based on the long-held belief that, once applied, the compound begins to rapidly decompose until all traces of it have either dissipated or broken down into relatively benign, inorganic bromides. Consequently, residues of such bromides are the only ones for which official tolerances were ever set, and testing for organic—or actual—methyl bromide has never been required, although its use in pest control dates all the way back to 1932.

At present, however, "most reliable scientists see no reason to run (tests for) inorganic bromides," observes American Spice Trade Association Executive Vice President Tom Burns. "They are no hazard. It's a waste of chemistry, time and money." And, having indeed found evidence of organic residues, the EPA is now just beginning to develop the voluminous data necessary to establish tolerances for methyl bromide per se in the numerous commodities on which it is used—a process whose projected time frame EPA representatives would not even venture to guess at.

In the meantime, any testing for the organic chemical in foods would have to be purely voluntary and may often not even be feasible. While it tests its products for other chemicals, for instance, the Gerber Baby Food Company, which uses methyl bromide at its Fort Smith, Ark., facility, has neither the "facilities" nor "analytical capability" to check for residues of the poison, according to a spokesman. "At this point," he adds, "we've been relying on approved use procedures."

The notion that methyl bromide fumigation leaves organic residues on anything is one that continues to be denied by the pesticide's chief manufacturer. "We have an extensive residue chemistry program well under way, and I can say without reservation that foods as consumed contain no detectable levels of methyl bromide," contends Dr. Vernon White of Great Lakes Chemical Company in West Lafayette, Indiana. "And, of course, if there's no exposure, there's no risk."

But Gary Obenauf, a spokesman for the California Raisin Advisory Board, Prune Board and Walnut Marketing Board, isn't nearly so confident. Based on preliminary data gathered by the California boards, he believes that amounts of the chemical are apt to be found in dried fruits and nuts, "probably in the neighborhood of a few parts per million." He also feels that the fumigant's future use is by no means assured. "Because we don't have a viable alternative, we're in a very precarious situation," he admits. "We don't know a lot and there are so many variables involved . . . we're flying by the seat of our pants at this point."

The variables to which he refers do indeed tend to complicate the residue issue. There is, for instance, the question of when and how many times a product may have come into contact with the toxin. Then there's the matter of temperature at which fumigated items are stored, since methyl bromide may persist longer under cool con-

ditions. (USDA regulations, in fact, often call for refrigeration as a prescribed condition of use.) Packaging is also a consideration, remembering the tendency of the gas to become "trapped." Finally, there's the all-important question of the kinds of commodities involved. According to Obenauf, products containing high oil and fatty acid, such as nuts, are likely to retain the chemical longer than others. One result was the insistence of Japanese authorities that shipments of fumigated nuts be held "for at least a month after treatment" before entering their country.

Further muddling the dietary exposure picture are the inconsistent ways in which corporate users handle methyl bromide in food processing plants. A spokesman for the Gerber Baby Food plant in Fort Smith, Arkansas, for instance, while acknowledging that the chemical is used on "most of (its) bulk flours and packaging materials," indicated that the company has reservations about using it on packaged products, since "there's some question of what happens" when "something is in the package and the package is treated." The Borden Company, on the other hand, empties all silos of raw material prior to fumigating its Prince Spaghetti plant in Warren, Michigan, but otherwise has no qualms about exposing "everything we make that happens to be on the premises"—that is products in corrugated boxes—to the gas, according to company representative Ottava Mecca. (The building's offices, however, are spared from fumigation as "it might be dangerous to the computers.")

Another major company, Kraft, acknowledges using the poison to control cheese mites in the storage area for its Parmesan cheese (the kind of product reportedly prone to residue retention), which, according to a company representative, is tested for inorganic bromides in accord with "industry practice." (Whether the cheese remains in the area during fumigation, however, is a point no one seems prepared to clarify.)

Then there's Pillsbury, whose use of the fumigant appears to be tempered by extreme reservation. "Methyl bromide is a chemical that we don't use on any food products," says Pillsbury spokesman Lane Paolocci in describing its application at the company's grain milling plant in Buffalo. "(It's) usually just used on fruits and vegetables, typically not on flour because of the potentials for residue . . . which is why we only do it on empty buildings." (Pillsbury, incidentally, recently settled a suit for an undisclosed amount against four insurance companies for lost business due to negative publicity arising from the suspension of EDB in 1983.)

Other food processors go beyond mere misgivings. The Planters Company—a Nabisco subsidiary—neither uses the chemical nor "allow(s its) use on the products we sell," according to a representative. And a spokesman for quality assurance at Kellogg's states quite emphatically that methyl bromide use is "not acceptable" by the company and is not allowed on any of its grain products or around any grain it buys—a policy in force prior to his joining the company 13 years ago.

The pest control industry's position, of course, is unequivocal. It holds that methyl bromide, when used as prescribed, not only poses no significant threat to the public, but is a virtually indispensable weapon in battling insects. One industry source—a spokesman for Western Fumigating—goes a step further in asserting that it represents the only means by which "the good people" of Chile can keep their economy viable and thus "continue their fight against communism."

Such advocacy might seem natural, but it is also particularly significant when one considers the industry's role in determining whether methyl bromide will ultimately be allowed to continue in its many existing capacities. For while it will require several years of extensive testing for the EPA to make up its mind, it is not that agency's job, however, to conduct such testing itself. "We put the onus on the registrant to give us the data—we don't care how they get it," says Jeff Kempter, an EPA team product manager. In this case, the registrant is considered to be the Methyl Bromide Industry Panel, chaired by Dr. White of Great Lakes Chemical. That organization, in turn, is currently looking to others for help—end user groups like the National Coffee and Chocolate Associations who "find methyl bromide to be highly important for their purpose," according to Kempter. It has even approached the USDA, hoping to "get some money there" from research funds, he claims.

By calling for a broad spectrum of specific tests, the EPA reportedly hopes to fill what it admits are "residue and toxicology data gaps" on methyl bromide which currently prevent the agency from considering "significant new food uses" for the chemical. An EPA fact sheet cites chronic toxicity, dietary and applicator exposure and groundwater contamination as among the areas in need of illumination.

Until it is provided, however, the EPA's official position is to continue to allow all currently registered products containing the poison to be "sold, distributed, formulated and used." Its stated rationale is that the agency "does not normally cancel or withhold registration for previously registered use patterns simply because data are missing or inadequate."

Just what does the EPA actually know about methyl bromide? That all seems to depend on what sources within the agency you consult.

The EPA's registration standard, for instance, refers to the chemical's "demonstrated mutagenic effects." These are also discussed in a report issued by an offshoot of its Office of Water and Waste Management. Another EPA document, the Profile for Extremely Hazardous Substances, cites such effects of chronic exposure as "severe and permanent brain damage."

However, to Walter Francis, the author of the EPA's official pesticide fact sheet on methyl bromide, such findings seem to some as news. "As of this time, I don't think any of the studies would point to that," he says.

In fact, his particular sector had so far failed to come up with "any adverse effects on any of the data we've looked at . . . no type of mutagenicity or chronic affects associated with it."

Ninety-nine percent of that data, he admits, comes from industry sources—meaning the Methyl Bromide Industry Panel—since "we have no research labs to speak of and we can't contract out (for) specific chemicals." Manufacturers of the compound are also required by law to notify the EPA should they become aware of potential adverse effects, he points out. "As far as I know, there hasn't been anything that's raised a red flag."

But Francis does suggest that those EPA reports, along with evidence of genotoxicity cited on Great Lakes Chemical's safety data sheet, be submitted to his office. "Otherwise, there would be no way for us to know that they exist."

When Dr. L.H.J.C. Danse and his colleagues from Holland's National Institute of Public Health and Environmental Protection began a three-month study on rats a few years ago, they were quite unprepared for either the results it would produce or the international scientific flap that would follow.

Danse, however, thinks he understands why the U.S. government scientists who had asked to view the slides from the study were in such a hurry to debunk his research team's interpretation of them.

"I knew at the time that there was very big interest in the U.S. about methyl bromide, because they had just forbid another compound (EDB), and they then said that methyl bromide was safe. So they were embarrassed to see those results."

By force feeding methyl bromide to rats via gavage, the Dutch group had initially hoped to establish a "no-toxic effect" level for the chemical in the forestomachs of the test animals. In their subsequent report on the experience, though, the researchers concluded that "because of the unexpected carcinogenic response in this 90-day rat study it is not possible to estimate a no-effect level based on a threshold dose." They also determined the chemical to be a "potent stimulus of cell growth which will promote a carcinogenic process." This was based on a finding of squamous cell carcinomas in 13 of 20 animals in the highest dose group, with all animals in the group exhibiting hyperplasia—a marked abnormal cell increase. Less pronounced hyperplasia was also observed in rats administered lower doses.

According to Danse, he and his colleagues "were very surprised to find these tumors in such a short study, and at the moment . . . had no plans of doing a reversal study." It was then, he says, that the group came into contact with Dr Gary Boorman, chief of the Chemical Pathology Branch of the National Institutes of Health at Research Triangle Park, North Carolina, who "asked us as a 'friend' institute to give (them) the slides and an opinion of these slides." The only discussion of the matter, he claims, involved whether "we should do that (second) study or they should."

At no time, he adds, did the Americans express doubts about his qualifications or "treat me in a way that indicated I did a wrong diagnosis."

Boorman's recollection of events, however, is somewhat at variance with the account provided by Danse. And while readily acknowledging that to produce such a cancerous reaction in just 90 days would indeed have been "tremendous," the evidence, he contends, simply wasn't there.

According to Boorman's scenario, his group became involved "after EPA asked us to evaluate the Dutch study and we had a friend of a friend talk to the person who's head of the Institute to give us the slides," which he then showed to a dozen pathologists from medical schools, pharmaceutical and chemical companies and the NIH.

When "the vote was zero for tumors," he contends, "we called them (the Dutch team) and asked them to publish a retraction or to send a letter saying that on second thought maybe it's not quite as strong or something, and they refused, so we thought we had no choice but to repeat the study. I haven't heard from them since."

"Our conclusion was that (what the Dutch researcher observed) was not really carcinoma; they misdiagnosed that," says Dr. Raymond Yang of the National Toxicology Program which was involved in the subsequent, somewhat lengthier study. "In such a short duration . . . the only thing they had seen is hyperplasia; they didn't see any cancer per se." In fact, he declares, to have a study of only three months' duration end up producing stomach cancer would be "highly unusual."

Which isn't to say that the Boorman group had determined "there was no evidence that methyl bromide is a rodent carcinogen, as the Industry Panel's chairman, Dr. White, maintains.

"I think he (Dr. White) is stretching the truth a little bit," says Yang. "As a scientist responsible for methyl bromide in the NTP, I certainly would not dare to make that sort of comment right at this minute . . . to make a blanket statement like that is inappropriate."

What the U.S. researchers did conclude was that 100 percent of the rats receiving methyl bromide continuously over a 25-week period developed hyperplastic lesions of the forestomach, a condition which "may or may not precede cancer," according to Dr. Yang. Furthermore, one rat in the group showed evidence of malignancy, the implications of which, while "not statistically significant, cannot be ignored," the published report on the American study noted. In fact, hyperplastic responses are usually characteristic of carcinogenic chemicals, Yang observed.

It isn't the outcome of the NTP study itself that Danse takes issue with, but rather the Americans' apparent attempts to discredit his own group's research.

Boorman, for instance, claims there were no pathologists involved in either conducting or reviewing the Dutch study—only graduate students and a toxicologist. To Danse, that is

"very peculiar and not very correct," as not only is he a qualified pathologist, but so were several other doctors who concurred with his findings—including Dr. Groth, the ex-NIOSH staffer. Groth confirms his role, recalling that "generally I agreed with the fact that they did produce tumors." And NIOSH, for its part, freely admits to having used the Dutch results in arriving at its own determination that methyl bromide is potentially carcinogenic.

Curiously enough, that's something the Dutch government has yet to do. But then, it really needn't bother, because, according to Danse, methyl bromide's use in the Netherlands is currently "restricted to a very few products—and then only at a single part per billion."

That, he says, is because, carcinogenicity aside, "it's not such a nice compound," but one that represents "a very serious risk for consumers and users."

Barb Troy remembers Terry Ray Schneider as a "fun-loving guy . . . real high-spirited." At 19, Schneider was assistant manager of the Village Inn, a popular Iowa City pancake house where Troy is employed as a waitress. He had been working there about eight months and was thinking of possibly making the restaurant business his permanent career when, sometime before 5 A.M. on October 6, 1988, any permanent career prospects he might have had were abruptly ended within the confines of the Village Inn.

With more responsibilities than usual on that particular morning, Schneider had been the first employee to arrive at work. In addition to restarting the computer, he also had to remove some plastic tarps from food coolers and other items. The tarps had been put down as a protective measure while Davenport extermination company performed a methyl bromide fumigation that had been completed shortly before midnight.

"I got here about five, and one of the girls was here before I was," Troy recalls. "We found his stuff up front—his coat, cigarettes and keys—but not him. We could see that he'd been in the office." It was at first assumed that Schneider was with the manager, she says, but when the latter showed up, "we didn't think about it again." That is, until a few minutes later when a cook found him lying on the floor of the men's room, where he had vomited and collapsed. He was dead on arrival at University Hospital.

Just how had the Village Inn managed to retain levels of methyl bromide sufficient to kill Terry Schneider? It had, after all, been thoroughly vented immediately following fumigation, hadn't it? Well, not exactly, according to the report from the Johnson County Medical Examiner. That report alleges that, in addition to the ventilation system not having been turned back on, some of the vents also remained covered with plastic. As a result, pockets of the chemical had probably built up in confined areas—such as rest rooms.

But why did the fumigator fail to detect this prior to allowing employees to reenter? As James Sargent, an entomologist with Great Lakes explains it, "the guy thought he was taking gas readings . . . he didn't know that he had put the tube in backwards." As for the blocked vents, "he thought that this kid had taken the plastic off the roof 'cause he's been told to do it, but he apparently didn't go up and check on it. . . . He was trying to do a job and . . . some unfortunate things took place."

Fumigating in the United States is currently a $100,000,000-a-year business, according to Joe Kaznicki's estimate. That figure, however, could grow even larger if the idea now being promoted by the firm for which Kaznicki works as an office manager in Lester, Pa., should begin to catch on.

It's an approach that the Western Fumigating Division of Western Termite and Pest Control is "just getting into selling" in the Northeast. The idea, Kaznicki says, is for free-standing restaurants to convert from the pest-control methods traditionally used in the region to fumigating with methyl bromide instead—a service that the Parsippany, N.J.-based company is now attempting to sell to the main offices of various fast-food chains.

It's a fairly simple proposition, he explains, which can be easily facilitated in a single night by tarping the restaurant after closing time, then reopening the next morning for business as usual. In fact, when dealing with a roach problem, he says, tarping may actually be unnecessary since not as much penetration of the gas is required.

While this may seem like a relatively expensive method of eradicating roaches, Kaznicki points out that with methyl bromide "they don't come back." Besides, "it's cheaper than having a customer see a roach on the table and walk out.

The firm has encountered some initial resistance, of course. That, he claims, is because in the Northeast where restaurant fumigating isn't customary, "people in the restaurant business don't like the idea of a deadly poison" being used in their establishments. To reassure them, however, Western representatives have been including in their presentation various testimonial letters attesting to customer satisfaction, he says.

Methyl bromide, after all, is the only fumigant still available that's approved for use around food, Kaznicki points out. And it's also one for which residue testing is unnecessary if it's "used according to the label."

Linda Bonvie and Bill Bonvie are a writer-research team based in Connecticut.

For further information on methyl bromide, contact the following organization:

United Farm Workers
Boycott Dept.
P.O. Box 62, Keene, CA 95531
(805) 822-5571

For further reading on methyl bromide, consult the following publication:

EPA Pesticide Fact Sheet #98
Aug. 22, 1986

METHYL BROMIDE (MBr) EMISSIONS

Total Impact Baseline consumption: 25,000 metric tons (tes)

Detailed Emissions Estimate

Use	Level		Emissions		Subtotal
Pre-plant	60%	x	25%	=	15%
Post-harv	30%	x	50%	=	15%
Structure	5%	x	100%	=	5%
Chemical	5%	x	0%	=	0%

TOTAL = 35% x 25,000 tes = 8,750 tes

8,750 tes x 0.6 ODP = **5,250,000 kg calc level**

Low Estimate

8% of pre-plant = 6,250 tes x 0.6 = **3,750,000 kg calc level**
[25% overall emissions]

High Estimate

40% of pre-plant= 11,250 tes x 0.6 = **6,750,000 kg calc level**
[45% overall emissions]

Currently Controlled Substances

Baselines in kg			ODP		kg calculated level
CFC-11	91,590,222	x	1	=	91,590,222
CFC-12	146,969,492	x	1	=	146,969,492
CFC-113	80,341,896	x	0.8	=	64,273,517
CFC-114	5,682,569	x	1	=	5,682,569
CFC-115	4,176,000	x	0.6	=	2,505,600
Hal-1211	2,961,971	x	3	=	8,885,913
Hal-1301	4,986,850	x	10	=	40,986,850
Group III	135,948	x	1	=	135,948
Group IV	67,531,900	x	1.1	=	74,285,090
Group V	31,494,057	x	0.1	=	3,149,406

Best Estimate

If 100% of MBr consumption equals emissions, then impact of MBr would be roughly 5 times greater than Group V (MCF). Best estimate (assuming only 35% total emissions) is that **impact of MBr is more than 1.5 times greater than that of MCF.**

November 25, 1991

Robert Watson

NASA Headquarters
Washington, D.C.

Dear Dr. Watson:

I am quite concerned about the recent finding of the WMO/UNEP Ozone Trends Scientific Assessment Panel, of which you are a co-chair, that "Methyl bromide is the major source of stratospheric bromine." Methyl bromide is, of course, a potent ozone destroying chemical, and the Assessment report as well as other reports in the scientific literature indicate that emissions of methyl bromide are largely anthropogenic in nature.

I would like to discuss this issue in detail. To that end, I would appreciate it if you could join me for a meeting in my office on December , at . Important issues include the state of our knowledge on the sources and sinks of methyl bromide; the volume of methyl bromide production and use in the United States and abroad; the principle uses of methyl bromide; and the availability of substitute chemicals. Dan Albritton and Susan Solomon from NOAA's Aeronomy Lab, Eileen Claussen from the Environmental Protection Agency, and several representatives of the methyl bromide manufacturing industry have also been invited to attend.

The latest findings on the rate, extent and duration of ozone depletion sound a loud warning that we must move ahead quickly in eliminating the production and use of ozone destroying substances. I therefore very much appreciate your willingness to participate in this discussion. I have included in this letter a copy of draft legislation that I would also like to discuss at our meeting.