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ATTACHMENT A
A-92-13
II-D-38

METHYL BROMIDE WORKING GROUP

May 14, 1992

Mr. David Lee, Branch Chief
Stratospheric Ozone Protection Program
Global Change Division, ANR-445
Office of Air and Radiation
U. S. Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460

FEB - 9 199?

Dear Mr. Lee:

This letter is submitted by the Methyl Bromide Working Group, in response to the request for information on methyl bromide, issued March 10, 1992 by Ms. Eileen B. Claussen, Director of the Office of Atmospheric and Indoor Programs at the Agency, under authority of Section 114 of the Clean Air Act. The Methyl Bromide Working Group ("the Working Group") is comprised of four companies: Ameribrom, Inc., Ethyl Corporation, Great Lakes Chemical Corporation, and Trical, Incorporated. Ameribrom, Inc., Ethyl Corporation, and Great Lakes Chemical Corporation manufacture all the methyl bromide used in the United States. Trical, Inc., is one of the largest distributors of methyl bromide.

The Methyl Bromide Working Group appreciates the opportunity to provide information on the question of methyl bromide and stratospheric ozone depletion. Over the past several months, The Working Group has been actively involved with the EPA in the issue of atmospheric methyl bromide. We had two meetings with the Agency to discuss the appropriate response to the petition filed on December 3, 1991 by the Natural Resources Defense Council and others. At those meetings, and in subsequent written communications with the Agency, the Working Group has offered to assist the EPA in resolving the question triggered by the December 3rd petition, whether methyl bromide should be regulated under Title VI of the Clean Air Act.

THE CLEAN AIR ACT AND THE MONTREAL PROTOCOL

The question whether methyl bromide should be regulated as a substance that contributes to the depletion of stratospheric ozone is being considered in two arenas: under the Clean Air Act and

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under the Montreal Protocol. Both of these deliberative processes require that decisions be based on sound science and adequate data.

A. The Montreal Protocol

The Working Group understands that each substance included in the Montreal Protocol was listed after the delegates determined that there existed a sufficient scientific basis to support the listing.

Indeed, the structure of the Montreal Protocol provides that particular substances be placed in a "transitional" category pending analysis of "scientific, environmental, technical and economic information". See Montreal Protocol Article 6. This approach ensures that the decision to include a substance in the Protocol is based on science, and it is well-suited to situations where existing data and analyses on the atmospheric effects of a substance are incomplete.

The Working Group believes that the position advanced by the Chilean delegation to the April 1992 meeting of the Open-ended Working Group in Geneva, is consistent with this tradition of demanding adequate science as the basis for adding suspected ozone-depleters to the Protocol. Under the Chilean proposal, the science base to support adding methyl bromide to the Protocol would receive two years of study.

B. The Clean Air Act

Like the Montreal Protocol, the Clean Air Act (CAA) provides that new substances be added to the Class I list pursuant to petition only in those situations where there is data adequate to support the listing. In particular, subsections 602(a) and 602(c) of the CAA provide that the Administrator can propose to list a substance as a Class I substance only where that petition presents data adequate to conclude that:

(i) the substance has an ozone-depletion potential ("ODP") of 0.2 or greater; AND

(ii) the substance causes or contributes significantly to harmful effects on the stratospheric ozone layer.

The Working Group recognizes that Section 602(a) of the Clean Air Act establishes the ODP value as only one criterion for including any given substance on the Class I list. However, the Working Group also notes that Section 602(a) of the Act directs the Administrator to consider in addition whether the substance

"cause[s] or contribute[s] significantly to harmful effects on the stratospheric ozone layer."

Given these separate statutory provisions, the Working Group believes it is entirely appropriate to examine all factors relating to methyl bromide (not merely its ODP) in reaching a regulatory determination under the Act. These factors would include the question of the sources and the lifetime of methyl bromide (including the issue of atmospheric sinks), as well as the relative contribution of man-made methyl bromide to the atmosphere as compared to naturally-occurring methyl bromide. In addition, other factors to consider include an understanding of the chemistry of brominated compounds in the atmosphere. In addition, the Working Group believes it would be appropriate to consider the importance of methyl bromide to crop production and food protection, and to reflect on the present lack of adequate alternatives, when considering the need for regulation.

In order to help ensure that substances are listed on the basis of the best available evidence, the Act expressly authorizes the Administrator to deny petitions where existing data are inadequate, and to use any information-gathering authority available to acquire that evidence.

In this respect, the Working Group would like to reemphasize the central points that were discussed in the course of our meetings and in written communications with EPA:
(1) the lack of scientific information relating to the effect of methyl bromide on the stratosphere (We discuss the specific scientific uncertainties relating to this question in the next section of this letter),
(2) the absence of any imminent threat from methyl bromide, and;
(3) the lack of adequate alternatives to the use of methyl bromide.

THE EPA DECISION-MAKING PROCESS UNDER THE CLEAN AIR ACT AND THE MONTREAL PROTOCOL

Representatives from the Working Group met on March 9, 1992 with Assistant Administrator for Air and Radiation William G. Rosenberg, Director Claussen, and their staffs to discuss the methyl bromide issue. During that meeting, Ms. Claussen and her staff advised that they were convinced that methyl bromide has an ODP greater than 0.2, and that the Agency intends to propose to list methyl bromide as a Class I substance on or before June 3, 1992 in response to the NRDC petition. This statement echoed similar statements made by Ms. Claussen at a December 18, 1991

meeting with Working Group representatives and in public forums elsewhere.

Moreover, the Working Group observed that at the April 1992 Open-Ended Working Group meeting held in Geneva, Switzerland, EPA staff took the position that methyl bromide must be included in the Protocol and its use eliminated by the year 2000. The EPA position was circulated to other members of the U.S. delegation to the Geneva meeting on or about March 18, 1992 and the EPA staff tried to convince/persuade the delegates to that meeting to adopt this position.

The EPA position on this issue thus appears to have been determined quite rapidly, and is apparently based largely upon a recent report by the United Nations Environment Program ("UNEP") which, at the end of last year, for the first time, identified methyl bromide as a substance that might have some ozone-depletion potential. Indeed, the Agency's Section 114 letter begins by reciting the "best estimate" of the ODP for methyl bromide contained in the December 17, 1991 UNEP "Scientific Assessment" as one reason for the request.

Given the weight EPA apparently grants to the UNEP report, the Working Group believes it important to note that the subject of methyl bromide was not discussed during the UNEP meeting held last October. Instead, the UNEP report's estimates on methyl bromide -- estimates which were not properly peer-reviewed in advance of publication -- were simply left unaddressed during that meeting.

In the view of the Working Group, these actions by EPA suggest either an unfortunate inclination to pre-judge the issue, or at a minimum a predisposition to move quickly to a decision on the phase-out or elimination of methyl bromide that simply is not warranted by the quality of the existing data and the unusual range of scientific uncertainty over the effect of man-made methyl bromide on the stratospheric ozone, that are discussed in the following section of this letter.

SCIENTIFIC UNCERTAINTY WITH RESPECT TO METHYL BROMIDE IN THE ATMOSPHERE

On February 10, 1992, the Working Group submitted a letter to Assistant Administrator Rosenberg, that summarized the scientific uncertainties associated with the question of whether man-made methyl bromide contributes in any material way to stratospheric ozone depletion. A copy of that letter is attached as Attachment I.

The range of uncertainty concerning the role of methyl bromide in the atmosphere is substantial. It is undisputed that the current range of uncertainty as to the effect of methyl bromide in the depletion of stratospheric ozone, far exceeds the level of uncertainty with respect to the role of CFCs and halons. These uncertainties pervade all aspects of listing methyl bromide.

Uncertainties relating to Atmospheric Chemistry and Lifetime

The range of uncertainties related to the atmospheric chemistry and lifetime of methyl bromide is sufficiently significant that it affects the ultimate conclusion as to whether there are grounds to list methyl bromide under the Clean Air Act. For example, the one point on which there appears to be scientific consensus is the fact that the lifetime in the atmosphere of methyl bromide is in the range of 1.2 to 1.8 years, compared to an estimated atmospheric lifetime of 80 to 300 years for some CFCs and halons. Thus, there is general agreement that any methyl bromide which enters the atmosphere is quickly eliminated.

However, while there is apparently scientific consensus that the atmospheric lifetime of methyl bromide is in the range of 1.2 to 1.8 years. This value is based on the assumption that OH is its only sink. The question remains unresolved whether there are additional significant sinks that would reduce the lifetime to less than 1.2 years. In the event the scientists conclude that the lifetime of methyl bromide is less than 1.2 years, serious questions are raised as to whether man-made methyl bromide contributes in any significant way to stratospheric ozone depletion.

In this regard, the Working Group understands that the EPA continues to assume that OH is the only possible sink for methyl bromide in the atmosphere. This assumption, too, is open to scientific dispute. For example, because methyl bromide is highly water-soluble, breaks down promptly in the presence of organic matter, and has a relatively weak C-Br bond, some scientists believe it is likely that removal processes other than OH exist. Thus, some methyl bromide is likely removed from the troposphere by rain and by contact between the air and organic matter in the soil. The significance of these removal processes remains to be determined. The existence of significant sinks in addition to OH would reduce the estimate for the atmospheric lifetime of methyl bromide.

In addition, estimates of the ODP for methyl bromide rest on certain unsubstantiated assumptions regarding the stratospheric chemistry of bromine. Scientists who have been deeply involved in

this area recognize that the understanding of stratospheric bromine chemistry is not well-developed, and that it is not nearly as complete as is the understanding of the stratospheric chemistry of chlorine. Based upon the current state of knowledge, the processes by which bromine reacts in the atmosphere are not necessarily the same as the processes by which chlorine reacts. For example, scientists currently assume that methyl bromide is photo-decomposed to form bromine after entering the atmosphere, and that the resulting bromine reacts through several possible pathways to produce BrO, Br_2, BrCl, $BrNO_3$, HOBr, and HBr. At present, the working assumption by many scientists is that the concentration of BrO should be in the range of 6 pptv under present conditions, while the concentration of HBr should be in the range of 1 pptv. However, the partitioning of Br into these various configurations is not well understood. Under the circumstances, more research is needed to be done to study the chemistry so that more accurate ODP estimates can be developed.

This lack of understanding of the chemistry is of more than academic concern. In fact, there is a potentially significant disparity between existing readings of HBr in the atmosphere and the assumptions as to bromine chemistry that have been used to predict the ODP for methyl bromide. Specifically, measurements of HBr by Dr. J. Park of NASA in 1989 suggest that stratospheric levels of HBr could be as high as 20 pptv (not the 1 pptv assumed on the basis of existing atmospheric chemistry models). If these readings are accurate, then significant questions arise, both as to the atmospheric chemistry of bromine and as to the magnitude of the total global level of methyl bromide from natural sources. This reading suggest that the ODP of methyl bromide could be significantly lower than estimated by the UNEP study.

The Working Group has observed that the Agency apparently prefers to discount the measurements taken by Dr. Park, and to rely instead upon certain other readings of HBr. Most recently, the Working Group was advised that government scientists also are relying upon certain measurements of BrO taken by Dr. Anderson as a means of questioning Dr. Park's results. However, the Working Group believes it important to note that Dr. Park's work was peer-reviewed prior to publication by a leading scientist in this field. By contrast, we understand that the measurements on which the Agency is relying have never been peer-reviewed. At a minimum, it seems reasonable to conclude that there is a need for further work in this area before the Agency reaches any conclusions.

One of the more striking aspects of the uncertainty surrounding this issue is that new data and analyses appear on virtually a weekly basis. In the period of time since the Working Group submitted its letter of February 10, 1992 to Assistant Administrator Rosenberg, the Group has been made aware of

additional stratospheric measurements by NASA, new "probability analyses" by NOAA, new measurements by scientists of "sinks" in the atmosphere, and other matters relating to the basic issue of the ozone-depletion capacity of methyl bromide. Many of these new matters have been discussed in the press. (See Wall Street Journal editorial - Attachment II, and Washington Times article - Attachment III). The press also has reported recently on the Agency's acknowledged need to improve the fundamental quality of its research efforts. (See New York Times article - Attachment IV).

Uncertainties Related to Sources of Methyl Bromide

There is similar uncertainty over the sources of methyl bromide. Unlike CFCs and halons (none of which occur naturally), a very significant percentage of the methyl bromide in the atmosphere is naturally-occurring. The available literature shows that some scientists believe as much as 80% (or more) of methyl bromide is naturally-produced. If these estimates are correct, control of man-made methyl bromide would have very little positive impact on stratospheric ozone.

In view of the lack of adequate scientific information on this issue, the Methyl Bromide Global Coalition is convening a major workshop on June 2 and 3, 1992 that will gather leading scientists from around the world to review the latest information on the potential effects of methyl bromide in the atmosphere. These scientists will bring to the workshop state-of-the-art knowledge on all aspects of this issue, including most recent information and analysis regarding:

(i) methyl bromide sources and emissions;
(ii) field measurements of methyl bromide concentrations in the troposphere and the stratosphere;
(iii) laboratory kinetics relevant to methyl bromide behavior in the atmosphere;
(iv) sinks for methyl bromide; and
(v) ozone-depletion potential ("ODP") modeling with respect to methyl bromide.

To date, more than two dozen eminent scientists, including the scientists from NOAA and NASA, have agreed to participate actively in this workshop, and the Open-Ended Working Group meeting in Geneva recommended that the workshop be included in the ongoing Montreal Protocol deliberations. The Global Coalition has also invited EPA staff to attend the workshop. On behalf of the Global Coalition, the Working Group reiterates that invitation here.

On March 20, 1992, the Working Group requested EPA, NOAA and NASA to provide all data relevant to these matters, but it has not

yet received a response. The workshop on June 2-3 will provide a good opportunity for the scientists of EPA, NASA and NOAA, to make their new data available, and for it to be peer-reviewed, studied and discussed, as needed before any determination can be reached on the question whether methyl bromide should be regulated.

Among the many new developments since early February when the Working Group submitted its letter to Assistant Administrator Rosenberg is the circulation to the general public of the UNEP "Scientific Assessment." The Agency has relied heavily on that Assessment in both its oral and written communications with the Working Group. Significantly, however, two of the key papers on which the Assessment relied to calculate an estimated ODP for methyl bromide apparently had not been published at the time the Assessment was released. In fact, as of the date of the Assessment, one of those papers had not yet been submitted for publication. The two papers are referenced at page 6-18 of the Assessment; both were coauthored by Dr. Solomon of NOAA. The Working Group believes that these papers should be peer-reviewed before they can be relied upon by the Agency. If they have not been reviewed yet, the June workshop may provide a good setting for that.

The purpose of the Workshop is to understand the current status of the knowledge and to design a research program that will fill the information gaps so that the Agency can resolve the question of whether methyl bromide should be regulated under Title VI of the Clean Air Act.

The Working Group has noted that there is no evidence of any imminent threat posed to public health or the environment by the release of man-made methyl bromide to the atmosphere. Thus, in view of the short lifetime of methyl bromide, and the fact that most of the atmospheric methyl bromide is naturally occurring, the Working Group believes that an immediate ban on production of man-made methyl bromide would have little positive effect on stratospheric ozone, and devoting the time now to reducing scientific uncertainty would pose no risk of near-term harm to the stratosphere.

The Working Group noted with interest the statement from President Bush on February 11, 1992, when he declared the intention of the United States to "consider recent evidence suggesting the possible need to phase out methyl bromide." The Working Group believes that the idea of the scientific workshop is consistent with the President's intention to give close consideration to all relevant evidence in deciding whether methyl bromide should be

regulated under the Clean Air Act or under the Montreal Protocol. This consideration should be deliberate. There is no imminent threat that would support a rush to judgment.

METHYL BROMIDE USES

In its letter of February 10, 1992 to Assistant Administrator Rosenberg, the Working Group summarized the numerous ways in which methyl bromide contributes to crop protection and production, preservation of foods, pest control, and the like. (See Attachment I).

In summary:

(i) methyl bromide can improve yields of certain crops by up to 500%, thereby reducing the need to develop additional lands (including wetlands);

(ii) methyl bromide protects crops against nematodes, fungus, and other pests and diseases without contaminating groundwater;

(iii) methyl bromide protects seedlings;

(iv) methyl bromide protects stored grain;

(v) methyl bromide use conserves water; and,

(vi) methyl bromide fumigation is required on virtually all U.S. imports of fruits and vegetables,to prevent the introduction of distructive pests into previously uninfested areas.

In summary, methyl bromide plays a vital role in crop production and protection, and produces numerous other environmental benefits, as it is the only fumigant that can be used for control of such a broad spectrum of problems.

Stated plainly, halting production and use of methyl bromide would create significant harm to a wide variety of people, located in this country and elsewhere. Among other adverse effects, banning methyl bromide would:

(i) reduce the yield of such crops as tomatoes, peppers, tree fruits, nuts, grapes, and strawberries, thereby increasing the cost of food to the United States consumer by an estimated $46,638,000,000 annually;

(ii) require that more land be cultivated in order to meet world food demands;

(iii) disrupt the progress made by developing countries to diversify their agricultural base;

(iv) severely curtail the $9,000,000,000 per year trade in vegetables and fruits imported into and exported from the United States;

(v) require the increased use of other fertilizers and pesticides that pose significant groundwater and surface water contamination concerns

(vi) inhibit programs to reduce global warming, by increase of the number of seedlings and size of land needed to produce timber, food and feed. This increase will be required to compensate for the loss now prevented by the protection of methyl bromide against pests and diseases;

(vii) allow the spread of devastating pests such as the giant Italian land snail, the Khapra beetle, and the Asian tiger mosquito, into new, previously uninfested areas.

LACK OF ADEQUATE ALTERNATIVES TO METHYL BROMIDE

In the letter of February 10, 1992 to Assistant Administrator Rosenberg, the Working Group emphasized that there are, at present, no adequate alternatives or substitutes for the many beneficial uses of methyl bromide. These uses include crop production and protection, as well as the protection of commodities and produce.

It is worth noting as well, that the process of developing alternatives to methyl bromide is time-consuming and costly. In fact, members of the Working Group, as well as governments and other producers and suppliers, have been engaged in serious research and development efforts to discover and produce alternatives to methyl bromide for over ten years, without success. This effort will continue. However, even if a viable alternative were to be discovered today, the process of developing and testing that alternative, and obtaining the government approvals necessary for its use, would consume about 10 years, and investment of about US$ 10 millions, before the EPA and the public can be assured that the new product does not pose other environmental or toxicological risks.

Nonetheless, until this effort is successful, any ban or phase out with respect to the production or use of methyl bromide would have significant adverse consequences that outweigh any potential advantages.

SPECIFIC ITEMS SUBMITTED IN RESPONSE TO THE AGENCY'S REQUEST FOR INFORMATION

As part of this response, the Working Group is attaching supplemental material that addresses the specific questions posed by the Agency's Section 114 request. The Agency should be aware that much of the data it seeks in those questions simply does not exist. This fact highlights the need for further study before the Agency can determine whether methyl bromide should be regulated under the Clean Air Act. Nevertheless, the Working Group has endeavored to provide as much information as possible in response to the Agency's request.

The following is a detailed list of the items that are submitted as appendices to this response.

A. Production and Use Data:

The Working Group is attaching a report on production and use of methyl bromide, that it commissioned in 1991 and that was completed on February, 1992.

B. Degradation, Breakdown, and Emission Data:

The Working Group is attaching a report of a modelling study that was performed in Louisiana State University. This report assesses the rate of emission of methyl bromide into the atmosphere that is associated with soil fumigation.

C. ODP and Related Issues:

The Working Group is attaching a study completed recently by Dr. Dak Sze that addresses the ODP issue.

Costs and Benefits of Phase-out and of Substitutes:

In addition to the points summarized in section IV of this letter, the Working Group is aware of a study that is being done by the U.S. Department of Agriculture on the costs associated with a phase-out of methyl bromide and the use of substitutes. We will submit this report to the Agency, as soon as we get a copy. The Working Group is unaware of

information relating to any potential benefits of a phase-out, or of benefits associated with substitutes to methyl bromide.

CONCLUSION

The Methyl Bromide Working Group appreciates the opportunity to provide information on the question of methyl bromide and stratospheric ozone depletion.

The Working Group believes that this submission, including the attachments, demonstrate that existing data and analyses are not adequate to support any regulatory decision to propose methyl bromide for inclusion on the list of Class I or Class II substances under Section 602 of the Clean Air Act. For this reason, the Working Group requests that EPA deny the petition filed by the NRDC and others on December 3, 1991 in its entirety, and that it embark upon additional studies designed to address the question of the contribution of man-made methyl bromide to stratospheric ozone depletion.

Very truly yours,

David R. Bouchard

David R. Bouchard
Chairman
Methyl Bromide Working Group

Attachments

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DRAFT

Effect of CH_3Br on Stratospheric Ozone

by

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November 1992

Submitted to Geophysical Research Letters

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Abstract

The much faster rate coefficient for the reaction of BrO + HO_2 (1) recently reported by Poulet et al. (1992) has important implications for stratospheric bromine chemistry. With this new rate coefficient, the calculated impact of bromine on stratospheric ozone could be significantly larger or smaller than previous estimates, depending mainly on whether HBr is among the products formed via (1). We present several models with different assumed rates for the HBr branch, and compare the calculated BrO_x species with available observations. Because of the scarcity of data for stratospheric bromine species, a 5-10% HBr branching cannot presently be ruled out. It is also noted that production of HCl via an analogous chlorine reaction ClO + HO_2 (2) could help resolve the discrepancy between models and observations (Stachnik et al., 1992). In view of the recent interest in CH_3Br, the major organic bromine in the atmosphere, we calculate its ozone depletion potential (ODP), the values of which, however, depend critically on the types of removal processes assumed in the model. Assuming tropospheric OH is the principal sink for CH_3Br, the calculated range of ODP is 0.24-0.85. The range reflects only the uncertainties associated with (1). Smaller ODP values (0.15-0.53) are obtained if we allow for additional CH_3Br removal by ocean. Removal by soil and vegetation could be important but is not included in the above ODP estimates.

1. Introduction

Tropospheric methyl bromide (CH_3Br) has been measured by several groups (WMO, 1992) who reported concentrations of about 10 to 20 pptv (1 pptv = 1 part in 10^{12} by volume) corresponding to a global abundance of 160-320 kilotons. With this level of abundance, CH_3Br is currently the major form of organic bromine of importance to the stratospheric budget. Although the impact of bromine chemistry on stratospheric ozone has been studied over the past decade (Wofsy et al., 1975; Yung et al., 1980; McElroy et al., 1986; Rodríguez et al., 1986), and more recently reviewed by Albritton et al. (1992), our knowledge of atmospheric bromine is less than that of atmospheric chlorine. There are, for example, far fewer observations of bromine species than of their chlorine counterparts. The only free bromine species which has been definitively measured is BrO over fairly restrictive altitudes ~15-20 km. Over polar regions, column abundances of BrO have been reported both from direct ground-based measurement (Carroll et al., 1989) and inferred from measurement of OClO (Solomon et al., 1987, 1988, 1989). Other bromine species, such as Br, HBr, HOBr, BrCl and $BrNO_3$ can only be inferred from model calculations. The very large variability (1-8

pptv) observed for BrO (Brune et al., 1988; Toohey et al., 1990) and the upper limits of 4 pptv set for HBr above 30 km derived from a few balloon flights (Traub et al., 1992) do not place stringent constraints on models of stratospheric bromine chemistry. The large differences between Park et al. (1989) and Traub et al.'s HBr also need to be resolved.

Assessment of the role of CH_3Br in stratospheric ozone is further complicated by the large uncertainties associated with its atmospheric budget. Unlike the CFCs and halons, there is little doubt that significant natural sources exist for CH_3Br (Wofsy et al., 1975; Singh et al., 1983; Albritton et al., 1992). The derivation of the atmospheric lifetime which is of vital importance to the determination of the ozone depletion potential (ODP), depends critically on assumptions on the magnitude of natural sources, its absolute atmospheric abundance, and removal processes.

One recent development in bromine chemistry concerns the new rate constant for the reaction

$$HO_2 + BrO \rightarrow HOBr + O_2 \quad (1a)$$

$$\rightarrow HBr + O_3 \quad (1b)$$

reported by Poulet et al. (1992) and recently recommended by JPL-92. With an estimated temperature dependence (JPL, 1992), the new rate is about a factor of 10 faster than that recommended by JPL (1990) at stratospheric temperatures. Reaction (1a) represents one of the rate limiting steps in the following bromine-HO_x catalyzed ozone loss cycle:

$$\left.\begin{array}{c} Br + O_3 \rightarrow BrO + O_2 \\ BrO + HO_2 \rightarrow HOBr + O_2 \\ HOBr + h\nu \rightarrow OH + Br \\ OH + O_3 \rightarrow HO_2 + O_2 \\ \hline \text{Net} \quad 2O_3 \rightarrow 3O_2 \end{array}\right\} \quad (I)$$

With the faster rate, reaction sequence (I) could be as important as the more commonly known catalytic cycle involving chlorine and bromine radicals (Yung et al., 1980):

$$\left.\begin{array}{l} Br + O_3 \rightarrow BrO + O_2 \\ Cl + O_3 \rightarrow ClO + O_2 \\ BrO + ClO \rightarrow Cl + Br + O_2 \\ \hline \text{Net} \quad 2O_3 \rightarrow 3O_2 \end{array}\right\} \quad \text{(II)}$$

However, as we shall show in later calculations presented in Section 2, any appreciable (>5-10%) production of HBr via (1b) or alternative HBr source (e.g., BrO + OH) could substantially lower the calculated BrO concentration and thus reduce the roles of both (I) and (II) in ozone loss.

The main purpose of this paper is to assess the implications of the faster rate for (1) and the possible HBr branching for the impact of bromine on ozone, specifically in connection to the ODP of CH_3Br. In particular, we shall address the relevant issues: i) whether the assumed 5-10% HBr production via (1b) introduces a major inconsistency between models and observations, and ii) whether there is any evidence for the analogous chlorine reaction to produce HCl via:

$$ClO + HO_2 \rightarrow HOCl + O_2 \quad \text{(2a)}$$
$$\rightarrow HCl + O_3 \quad \text{(2b)}$$

In this paper, we shall show that there remain considerable uncertainties associated with the calculated ODP values for CH_3Br. Further quantification of removal processes (particularly for processes pertaining to surface removal), as well as measurements of several rate data (in particular (1a) and (1b)) at stratospheric temperatures, together with selective (e.g., HBr, BrO, etc.) atmospheric measurements, will substantially narrow the uncertainty range presented here.

2. Calculated Distribution of Stratospheric Bromine Species

In order to study the implications of the new rate data for stratospheric bromine chemistry, we consider four models (A-D) defined by different rates assumed for (1a) and (1b). Models B, C, and D adopt the new (faster) rate measured by Poulet et al. (1992) with the temperature dependence recommended by JPL-92:

$$k_1 = k_{1a} + k_{1b} = 6.2 \times 10^{-12} \exp(500/T) \text{ cm}^3\text{s}^{-1}$$

Model A assumes the slower rate of $5 \times 10^{-12} cm^3 s^{-1}$ with no T-dependence (JPL, 1990). Both models A and B assume no HBr production (i.e., $k_{1b} = 0$), whereas models C and D assume HBr production of 10% (i.e., $k_{1b}/k_1 = .1$) and 5% (i.e., $k_{1b}/k_1 = .05$) respectively. Our approach is to present vertical profiles for key bromine species in each of the above models and to look for any consistency and/or inconsistency between various models and available observations.

Figure 1 shows the calculated vertical profiles for the bromine source gases CH_3Br, halon 1201 (CF_2BrCl), and halon 1301 (CF_3Br) together with that of the total inorganic bromine BrY (Br + BrO + HBr + HOBr + $BrNO_3$, BrCl) that originates from the photodegradation of these three known bromomethanes. The calculated stratospheric abundance of BrY is about 15 pptv at ~20 km and approaches a constant mixing ratio of 19 ppt above 30 km. This feature of the model (except perhaps for the absolute magnitudes of the source gases) is similar to those predicted by Wofsy et al. (1975) and Yung et al. (1980).

Partitioning of BrY in the lower stratosphere depends on assumptions for heterogeneous reactions. The effect of heterogeneous reactions on sulfuric acid particles are parameterized as discussed in Rodríguez et al. (1991) as updated in chapter 8 of the WMO (1992) report. Briefly, the following reactions

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$
$$ClNO_3 + H_2O \rightarrow HNO_3 + HOCl$$

are assumed to occur with reaction efficiency of 0.1 and 0.006exp(-0.15(T-200)) respectively. The temperature dependence used in the second reaction is to reflect the dependence on the water content of the aerosol. The surface area for the aerosol correspond to the baseline lower limit case cited in WMO (1992). Figures 2a, b, c and d illustrate the sensitivity of models (A-D) to the rates adopted for (1) and to the assumed HBr branching (1b). Using the slower rate for (1a) (model A), the major forms of BrY are BrO and $BrNO_3$ with almost equal abundance in the important altitude region, 18-24 km (Figure 2a). The calculated concentration of other bromine species Br, HOBr and HBr are more than an order of magnitude lower than either BrO or $BrNO_3$. However, with the faster rate for (1a) (model B), the calculated abundance of HOBr approaches those of BrO and $BrNO_3$ (Figure 2b). Compared to Figure 2a, the calculated abundances for BrO and $BrNO_3$ (in Figure 2b) are lower because a faster rate for (1), on balance, tends to favor HOBr at the expense of BrO. In both models A and B (Figures

2a and 2b), however, the concentrations calculated for HBr remain well below 1 pptv. Figures 2c and d show a vastly different partition when we allow for HBr formation at rates adopted by models C and D. The calculated HBr (model C) reaches a maximum concentration of 10 pptv at around 22 km but decreases to about 6-7 pptv at 32 km, a region where Traub et al. (1992) reported a weighted average 1-σ upper limit of 4 pptv. With $k_{1b}/k_1 = 0.05$ (model D, figure 2d), the calculated HBr at 32 km lies below Traub et al.' s upper limit and the calculated BrO of about 2-3 ppt near 20 km also appears to be broadly consistent with observations taken at mid-latitudes (Toohey et al., 1990). While the Traub et al. upper limit places a useful constraint on HBr chemistry, the possibility of a HBr branch of ~5-10% cannot be ruled out in view of the expected temporal and spatial variability of HBr and the relatively small samples of data from which the upper limits are derived. Simultaneous measurement of both HBr and BrO in the lower stratosphere (~20-25 km), where HBr data is lacking and bromine is thought to play a more important role, would place much more stringent constraints on bromine chemistry.

Although there is no quantitative determination of (1b), there is laboratory evidence for appreciable HCl formation (Kuo et al., 1987) from an analogous reaction, $HO_2 + ClO$ (reaction 2). The HCl branch (2b) was found to be about 10-20% (Y.P. Lee, unpublished data, 1988, 1990), although other measurements (JPL-90) indicated negligible HCl production. Figure 3 compares the calculated ClO/HCl ratios with the recent simultaneous measurements reported by Stachnik et al. (1992). Stachnik et al. (1992) noted that models tend to overstate the ClO/HCl by a factor of 2 or more in the mid-stratosphere. Because of the sensitivity of the ClO/HCl ratio to CH_4 distributions, we fixed the CH_4 concentrations using data from the SAMS instrument on the NIMBUS satellite (Jones and Pyle, 1984). Without invoking the HCl branching (i.e., $k_{2b} = 0$), our model calculations (Figure 3) agree with the Stachnik et al. assessment that the largest discrepancy occurs at around 30-40 km, a region where photochemistry is thought to be well understood. This discrepancy may be largely resolved if we invoke an HCl branch of 0.1 (Figure 3). Note that the comparison here involves the ratio of two reactive species (ClO/HCl) which, unlike most other quantities, is expected to be less sensitive to transport parameters and total chlorine abundance (ClY) in the model. Thus, it is unlikely that the discrepancy can be attributed to an inadequate model representation in atmospheric transport/circulation or to the chlorine abundance. Also, with the smaller ClO/HCl, the model calculated somewhat higher O_3 around 40 km and a smaller decadal downward trend for upper stratospheric ozone, bringing model calculations closer to satellite observations (McCormick et al., 1992; Hilsenrath et al., 1992). A more accurate determination of k_{2b} is clearly needed to ascertain the roles of (2) in defining the ClO/HCl ratio and other important quantities in the mid-upper stratosphere.

3. ODP for CH_3Br

The Ozone Depletion Potential (ODP), first introduced by Wuebbles (1983), is now extensively used by policy makers as a simple relative measure to assess the potential impact of a given compound on the stratospheric ozone layer. The ODP is calculated relative to CFC-11 and depends principally on two major factors: a) the calculated atmospheric lifetime, and b) the relative catalytic efficiency (α) in stratospheric ozone removal. More recently, Solomon and Albritton (1992) introduced the concept of a time-dependent ODP (TDODP). They noted that, over shorter time horizons, the TDODP for short lived species can be substantially larger than the steady state ODP currently adopted by parties to the Montreal Protocol. The relation between TDODP and ODP for a compound x may be expressed by:

$$\frac{TDODP}{ODP} = \frac{\tau_{CFC\text{-}11}}{\tau_x} \frac{\int_0^t e^{-t/\tau_x} dt}{\int_0^t e^{-t/\tau_{CFC\text{-}11}} dt} \qquad (3)$$

where $\tau_{CFC\text{-}11}$ and τ_x are the atmospheric lifetimes for CFC-11 and compound x respectively. In what follows, we will present calculations on ODP for CH_3Br under a variety of assumptions on τ_{CH_3Br} and the rate constants for (1a) and (1b).

a. Atmospheric Lifetime of Methyl Bromide

The net atmospheric lifetime (τ_{tot}) for methyl bromide is given by:

$$\frac{1}{\tau_{tot}} = \frac{1}{\tau_{gas}} + \frac{1}{\tau_{ocean}} + \frac{1}{\tau_{land}} \qquad (4)$$

In the above expression, τ_{gas} denotes the lifetime against atmospheric removal by gas-phase reactions and photolysis of CH_3Br, and is defined by the total column density (cm^{-2}) divided by the integrated loss rate ($cm^{-2}s^{-1}$) over the whole atmosphere. The lifetime against ocean uptake, τ_{ocean}, is defined as the methyl bromide atmospheric burden divided by the flux into the ocean. A similar definition holds for the lifetime against uptake by land surfaces, τ_{land}.

Although photolysis and reactions of CH_3Br with $O(^1D)$, $O(^3P)$, NO_3, and Cl take place in the atmosphere, gas-phase removal of methyl bromide is likely to be dominated by its

reaction with tropospheric OH. Based on the latest measurements of the reaction of CH_3Br with OH (Mellouki et al., 1992), of CH_3CCl_3 with OH (Talukdar et al., 1992), together with the most recent analysis of ALE/GAGE data (Prinn et al., 1992) a lifetime constant $\tau_{OH} = 2.1 \pm 0.5$ years, is derived. The quoted error only reflects uncertainties in the ALE/GAGE analysis.

Although certain regions of the ocean can be a net source for methyl bromide in the atmosphere, hydrolysis and reaction with chloride ions in sea water can also constitute an important sink for atmospheric CH_3Br. This is in contrast to halocarbons and proposed substitutes which, due to low solubility (typically $H \sim 10^{-2}$ moles/l/atm)and aqueous degradation rates (typically $k_w \sim 10^{-9}$ s^{-1}), have ocean uptake lifetimes of order of hundreds of years (Wine and Chameides, 1990). Using the stagnant-layer model for ocean uptake (see, e.g.., Liss, 1983), the lifetime against ocean uptake can be estimated from the expression (Wine and Chameides, 1990)

$$\tau_{ocean}(s) = \frac{H_A}{(H)(0.04)(0.7)} \{r_s + (Dk_w)^{-\frac{1}{2}}\} \qquad (5)$$

In the above, H_A denotes the atmospheric scale height (8 km), and D is the one-dimensional eddy coefficient in the oceanic mixed layer (top 100 m), $D = 40$ cm^2s^{-1}. We use a value of 0.15 moles/l/atm for the Henry's constant H (Mackay and Shiu, 1981; Elliot, 1985). The first-order aqueous degradation constant k_w includes contributions from both hydrolysis, and reaction of methyl bromide with chloride ion. We adopt a value of 3×10^{-7} for the hydrolysis rate at 22°C (Mabey and Mill, 1978), although values as high as 9×10^{-7} s^{-1} have been reported by Gentile et al. (1989). The chlorination rate at 22°C is taken to be 1×10^{-6} s^{-1} (Elliot, 1985). For the adopted value of H, diffusive transport is dominated by transport through the liquid stagnant layer (Wine and Chameides, 1990). A value of 255 s cm^{-1} is adopted for the liquid resistivity r_s; this value is obtained by scaling the value obtained from $^{14}CO_2$ value (180 s cm^{-1}; Liss, 1988) by the ratio of the square root of molecular weights. With the above assumptions, a value of $\tau_{ocean} = 3.8$ years is estimated.

For the adopted values of the aqueous degradation rate k_w, the terms on the right hand side of (5) are of comparable magnitude. The parameter r_s is very uncertain and variations of factors of two or more, depending on local meteorological conditions, are expected (see Watson et al., 1991). Since both chlorination and hydrolysis rates exhibit a large temperature dependence (Elliot, 1985; Mabey and Mill, 1978), more detailed calculations are also needed to further constrain the role of the ocean (see, e.g., Anber and Yung, 1992).

Measurements of deposition velocity of CH_3Br over land are not available. We note that a land surface deposition velocity of 0.03 cm/s would yield uptake lifetimes comparable to the ocean uptake. Such deposition velocities cannot be ruled out (Kolb and Harriss, private communication, 1992); however, given the lack of data, we did not include this term in our lifetime estimate (i.e., τ_{land} is set equal to ∞ in the estimation of τ_{tot}). Inclusion of τ_{land} will reduce τ_{tot}.

Combining τ_{gas} with τ_{ocean}, we estimate $\tau_{tot} \approx 1.3$ *years*

b. Calculation of Ozone Depletion Potential

We used the AER 2-D model with the standard JPL (1992) set of reaction rates for the gas-phase reactions and parameterization for heterogeneous reactions as described in section 2. For the calculation, we did not include heterogeneous chemistry due to polar stratospheric clouds. Following the method used in WMO (1992), the ODP is calculated based on a background chlorine and bromine concentration of 3.5 ppbv and 19 pptv, respectively. The ODP values were calculated using the bromine chemistry models (A-D) as discussed in Section 2.

The results of these calculations are shown and compared in Table 1. The third column in this table contains the calculated ODP, assuming only gas-phase atmospheric removal (lifetime of 2.1 years). The impact of ocean uptake is illustrated in the fourth column, where a total lifetime of 1.3 years is assumed). Inclusion of any land surface removal will further lessen the calculated ODP values. However, no attempt is made to include this effect because of current lack of meaningful data.

Table 1
Model calculated values of ODP for CH_3Br.

Case	Description	ODP, lifetime of 2.1 years	ODP, lifetime of 1.3 years
A	Gas-phase chemistry + heterogeneous reactions, JPL-92 except for BrO+HO2	0.64	0.40
B	Gas phase chemistry and heterogenous reaction, JPL-92	0.85	0.53
C	B + 10% branching for production of HBr in the $BrO + HO_2$ reaction	0.24	0.15
D	B + 5% branching for production of HBr in the $BrO + HO_2$ reaction	0.4	0.24

In addition to the uncertainties associated with the BrO + HO_2 reactions, there are large uncertainties associated with rate data for other key bromine reactions. For instance, the reaction rate of BrO + O3 is given as an upper limit with $k < 8 \times 10^{-14}$ cm^3 s^{-1}. However, the reaction could have a large impact on the calculated ODP if the actual rate approaches the upper limit. The rate constant was set to zero in our calculation. In order for $BrNO_3$ operative as an ozone depletion cycle, $BrNO_3$ must photo-dissociate into Br and NO_3. However, no measurements have been made (JPL, 1990) regarding the different possible photolysis products. If alternative dissociation paths exist, such as

$$BrNO_3 + h\nu \rightarrow BrO + NO_2$$
$$BrNO_3 + h\nu \rightarrow BrNO_2 + O$$

the reaction sequence for formation of $BrNO_3$ will become a null cycle (i.e., no impact on ozone removal). In our calculation, we assume a 100% yield for Br and NO_3.

Other key reactions for which rate constants are uncertain by at least a factor of two include the reactions of BrO with OH, O and NO2 and the reaction of Br with HO_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 bromomethanes including CH_3Br.

4. Concluding Remarks

The new rate for (1) substantially changes the partition between various stratospheric BrOx species. As a result, the BrOx-HOx cycle (I) could potentially become as important as the BrOx-ClOx cycle (II) in the model calculation of global ozone loss. However, the faster rate also implies that, even with a small (5-10%) HBr product branching, reaction (1) could constitute a major source of stratospheric HBr. Although data for (1b) are not available, there are indications (Kuo et al., 1987) that the analogous chlorine reaction may produce HCl (2b) in addition to HOCl (2a). We note that an additional source of HCl [such as (2b)] could help explain the recently published ClO/HCl ratio (Stachnik et al., 1992) and perhaps the slower observed O_3 trend in the mid-upper stratosphere (McCormick et al., 1992; Hilsenrath et al., 1992).

In contrast to the vast amount of data on ClOx species, observation of BrOx species are few. Although observations of BrO in the lower stratosphere and the tentative upper limits on

HBr above 30 km place some constraints on bromine chemistry, they do not rule out models which assume a small (5-10%) HBr branching. Laboratory studies of reactions (1) and (2) together with selective (but more frequent) stratospheric measurement (e.g., simultaneous measurement of BrO and HBr over an extended (20-30 km) altitude region) will help accelerate our understanding of stratospheric bromine chemistry.

The calculated ODP for CH_3Br depends not only on stratospheric bromine chemistry, but also on the calculated atmospheric lifetime. The processes which define the surface removal are not yet well understood. Thus, it is not even possible to quantify the range of uncertainties associated with these processes. Because ocean uptake is sensitive to both meteorological and ocean parameters, a detailed analysis of the variability of ocean uptake rate is needed. While there are some data to allow us to make a rough estimate of lifetime due to ocean removal, data on surface removal by soil and vegetation are currently lacking for meaningful estimates for the atmospheric deposition rates of CH_3Br. The wide range of ODP values calculated here can be narrowed by concentrated efforts on laboratory and field studies outlined by Albritton et al. (1992).

Acknowledgments

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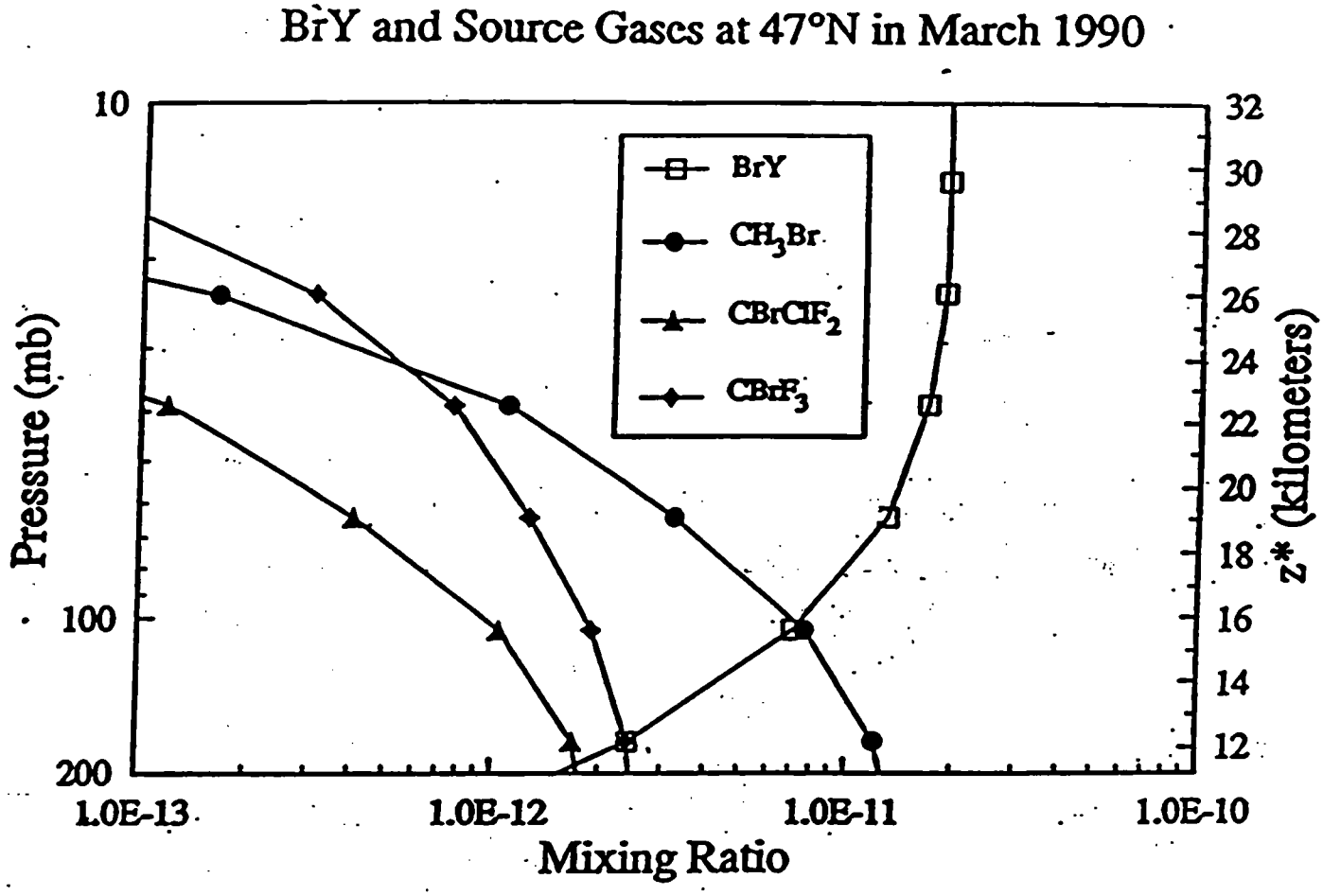

Figure 1. Model calculated vertical profiles of mixing ratio at 47°N in March 1990 for BrY, CH_3Br, $CBrClF_2$, and $CBrF_3$.

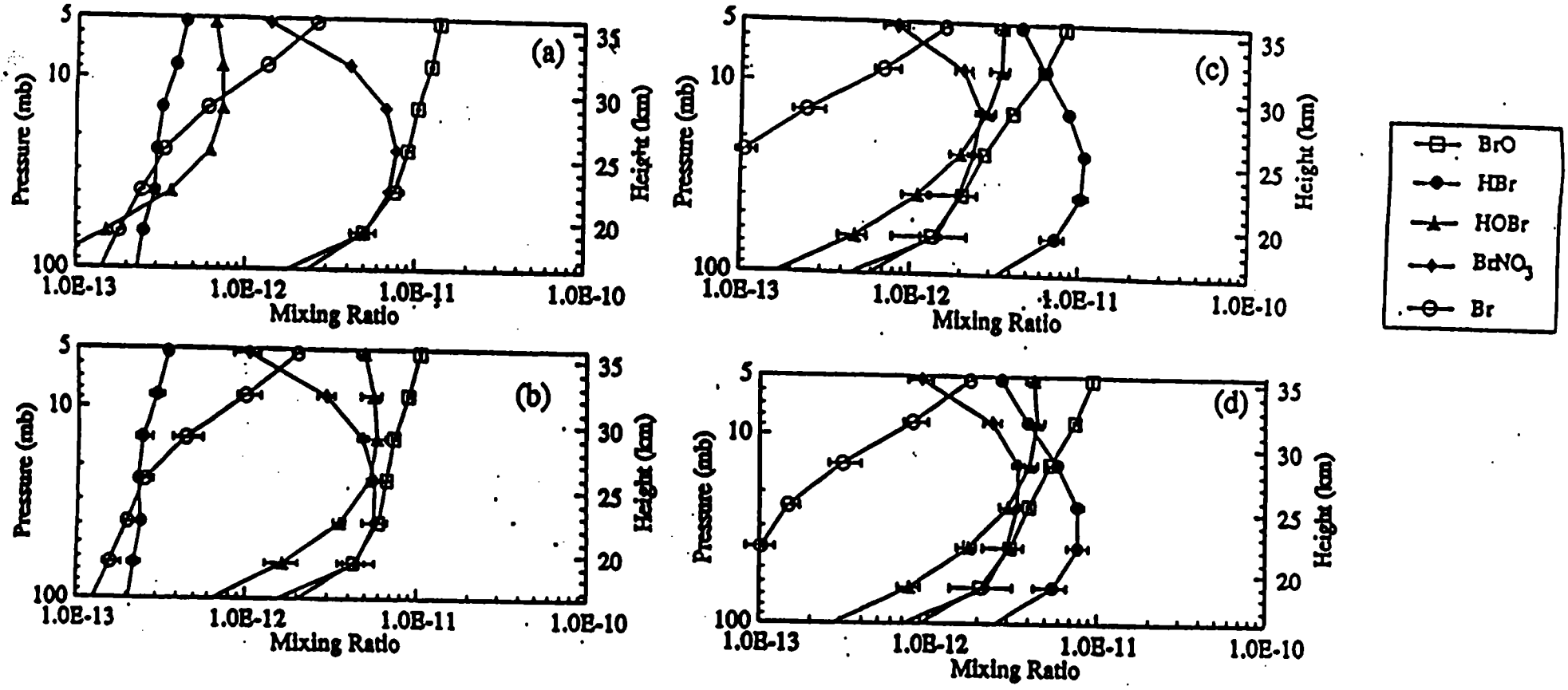

Figure 2. Vertical profiles of calculated mixing ratios of the odd bromine species at 38°N for 1990 annual average conditions with heterogeneous reactions on the sulfate layer included. The bars reflect the seasonal variations of the species. Results from the four models A-D are shown in panels a-d, respectively. The rate for BrO + HO_2 is taken from JPL-90 for model A while models B, C and D use the JPL-92 rate. Models A and B assume there is no HBr production from the reaction. Models C and D assume a 10% and 5% production of HBr, respectively.

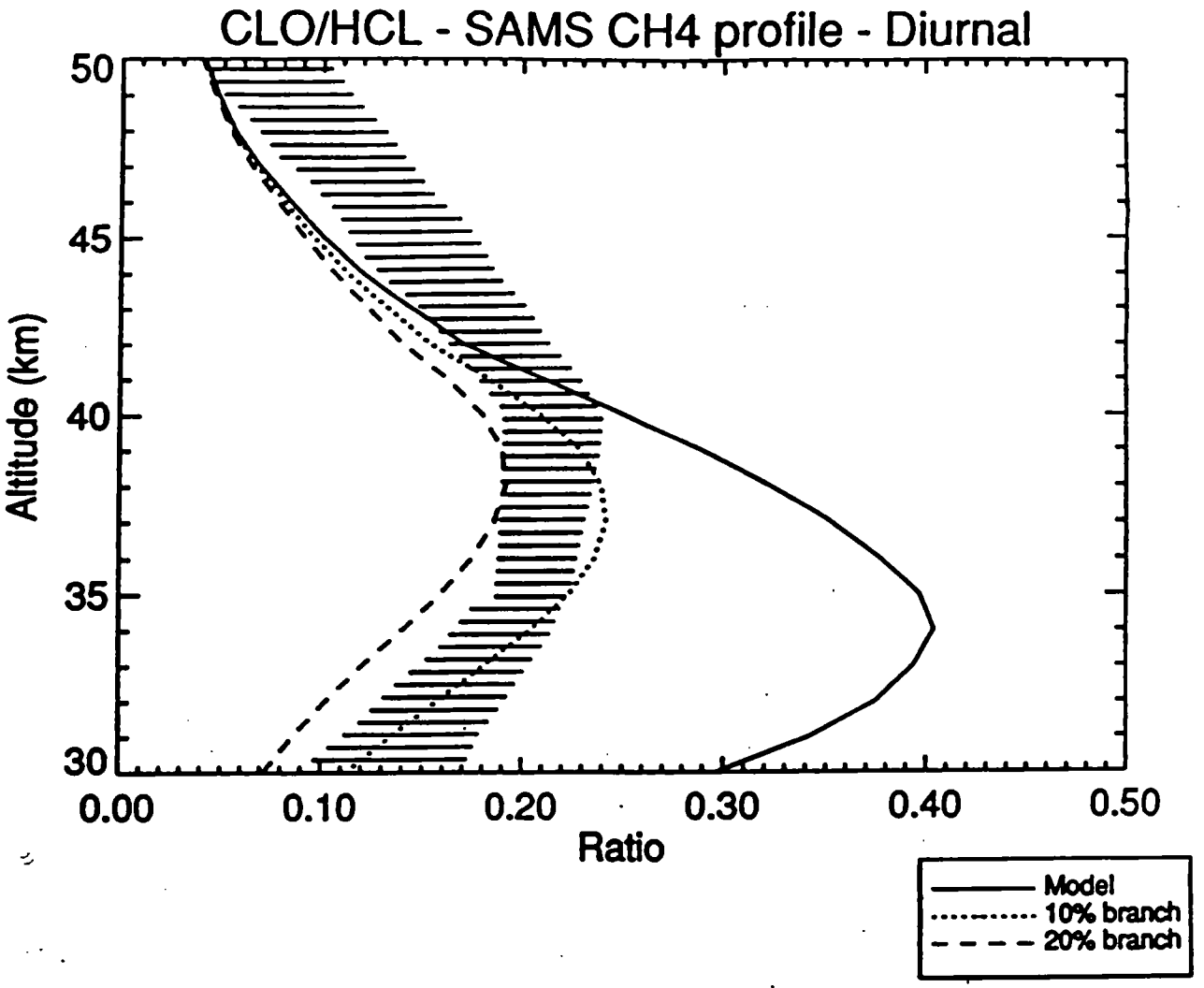

Figure 3. Model calculated ClO/HCl ratio together with observations (shaded regions) from Stachnik et al. (1992). The model results are calculated for 30°N conditions for March. The CH_4 concentration is taken from SAMS (Jones and Pyle, 1984). The curves are: (——) no production of HCl; (·····) 10% production of HCl and (– – –) 20% production of HCl, respectively, from the reaction $ClO + HO_2$.

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May 13, 1993

Dr. Tom Duafala
TriCal, Inc.
8770 Highway 25
Hollister, CA 95023

Dear Tom:

This a response to your request to estimate the effect on the calculated atmospheric lifetime and ODP of CH_3Br if it is assumed that the removal by soil has a lifetime of 3.8 years, comparable to the lifetime for ocean removal. The estimates are summarized in the table below.

Model calculated values of ODP for CH_3Br.

Case	Description	ODP, lifetime of 2.1 years	ODP, lifetime of 1.3 years	ODP, lifetime of 1 year
A	Gas-phase chemistry + heterogeneous reactions, JPL-92 except for $BrO+HO_2$	0.64	0.40	0.31
B	Gas phase chemistry and heterogenous reaction, JPL-92	0.85	0.53	0.41
C	B + 10% branching for production of HBr in the $BrO + HO_2$ reaction	0.24	0.15	0.11
D	B + 5% branching for production of HBr in the $BrO + HO_2$ reaction	0.4	0.24	0.19

Yours sincerely,

Nien Dak Sze

840 MEMORIAL DRIVE, CAMBRIDGE, MA 02139-3794
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Methyl Bromide Global Coalition

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May 18, 1993

THE METHYL BROMIDE RESEARCH PROGRAM

The purpose of the Methyl Bromide Global Coalition (MBGC) Research Program is to resolve scientific uncertainties surrounding the significance of man-made methyl bromide to ozone depletion. All of the research projects listed below will be completed in two to three years. This accelerated completion schedule is necessary because research going beyond two to three years would have little impact on the decisions of policy makers.

The research program includes studies in bromine chemistry, atmospheric measurements, natural sources of methyl bromide, sinks for methyl bromide, emission reduction, and modeling of the new data to access the impact of anthropogenic methyl bromide in ozone depletion.

A. BROMINE CHEMISTRY

BACKGROUND: Once organic compounds such as methyl bromide enter the stratosphere, they

decompose to release bromine atoms. There are several reaction pathways that bromine atoms can follow in the stratosphere. It has been suggested that one of these pathways produces HBr as an ozone harmless end product. If this suggestion is correct, there would be a significant reduction in the potential of methyl bromide to deplete ozone, thus reducing methyl bromide's calculated ODP.

There are two studies supporting the potential production of HBr. One is a report of Park et al, (1989), indicating that HBr was measured in the stratosphere at an altitude of 28 Km. In addition, Kuo, et al, (1987), reported that there is an analogous reaction for chlorine compounds where HCl is produced under laboratory conditions in the gas phase. If only ten percent of the bromine from methyl bromide went to HBr, this would in effect lower methyl bromide's calculated ozone depletion potential from 0.74 to 0.25. Laboratory research in this area should take 12 - 24 months to complete.

Two kinetic studies are being funded by the Methyl Bromide Global Coalition:

1. Dr. Mario J. Molina of the Massachusetts Institute of Technology proposes to carry out a laboratory investigation of the reaction between BrO and HO_2 with particular emphasis on product analysis; that is, on the production of HBr. Furthermore, he will carry out these studies at stratospherically relevant temperatures.

   The technique to be employed is atmospheric pressure fast flow (APFF), coupled to atmospheric pressure chemical ionization mass spectrometry (APIMS). Dr. Molina's laboratory developed the APFF technique as an extension of the well established discharge flow or fast flow method which in its conventional version is limited to low pressures; i.e. below about 10 torr. A major advantage of the higher pressure technique is that wall effects are greatly minimized: this is a crucial requirement for the investigation proposed here, because the most likely artifact in the generation of HBr involves wall reactions. These reactions are particularly troublesome at low temperatures,

which enhance heterogeneous reaction probabilities.

The fast-flow technique is particularly well suited for the study of radical-radical reactions such as $BrO + HO_2 \rightarrow HBr + O_3$, because of its versatility in terms of the clean generation of free radicals. For example, BrO can be produced by the reaction of Br atoms with ozone, the Br atoms in turn being generated in a microwave discharge. Similarly, HO_2 can be produced in various different ways; e.g., with F-atoms plus hydrogen peroxide, or H-atoms plus molecular oxygen (particularly at the higher pressures available to the APFF technique). The radicals are eventually mixed downstream in the flow tube and can be independently titrated.

MBGC will fund this project at $151,000 and it will be completed in twenty-four months.

2. Dr. Gilles Poulet and Dr. Georges LeBras of the French National Center of the Research Scientific Laboratory propose to measure the

rate constant for the reaction BrO + HO_2 at temperatures relevant to the stratosphere (at least down to 230 K) as well as the potential branching channel for HBr.

These researchers feel that, "the assumed possible formation of HBr at low temperatures is realistic considering the 'anomalous' temperature dependence observed for the Cl + HO_2 reaction, which can be interpreted by the occurrence of a change in the mechanism (Stimple et al., J. Chem. Phys., (1979) 71,5187), even if HCl has not been detected - up to now - in this analogous reaction."

The kinetic and mechanistic experiments will be performed in the same apparatus as that used in their recent studies of the reactions BrO + HO_2 and IO + HO_2 at 298 K. The discharge flow reactor associated with a molecular beam mass spectrometer will be surrounded by a jacket through which cold ethanol will flow. BrO will be produced from the reaction:

$$O + Br_2 \rightarrow BrO + Br \quad (1)$$

Two sources of HO_2 can be used:

$$Cl + CH_3OH + O_2 \rightarrow HO_2 + HCl + H_2CO \quad (2)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (3)$$

Reaction (3) will be preferred if the chemical system used in reaction (2) does not operate at the lowest temperatures.

MBGC will fund this project at $60,000 and it will take one year to complete.

B. STRATOSPHERIC MEASUREMENTS

BACKGROUND: If ten percent HBr is produced from the reactions BrO + HO, then you could expect to measure 2 to 6 parts per trillion HBr in the lower stratosphere. Previous HBr data was generated on instrumentation which had a minimum level of detection in the range 4 to 8 parts per trillion. Recently, analytical instrumentation has been improved and can now measure HBr at the 1 part per trillion level of detection. New measurements with improved instrumentation need to be taken in the lower stratosphere (less than 25 kilometers) where the actual reaction processes take place.

Another approach to looking at the production of HBr in the stratosphere is a reanalysis of existing BrO data. As levels of HBr increase in the stratosphere, then the current model calculated levels of BrO (8 PPT) would decrease. Currently, data indicate that the range of BrO measurements is from 2 to 10 parts per trillion. It is not known whether this range in values reflects the range in absolute values in the stratosphere or variations in calibration standards used by different individuals at different times. If the 10% HBr shunt occurs, then models predict only 4 - 6 parts per trillion BrO in the lower stratosphere.

Three research projects will be funded to investigate HBr production in the stratosphere. The first is a measurement of HBr in the lower stratosphere with the newer instrumentation. Two other projects involve a reanalysis of BrO measurement data using better calibration standards.

1. An international team composed of Dr. Ira Nolt of NASA Langley Research Center; Drs.

Peter Ade and Matthew Griffin of Queen Mary and Westfield College, London; and Dr. Bruno Carli of Italy proposes to develop accurate measurements of stratospheric HBr using a balloon-based Fourier transform emission spectrometer. The unique advantage of the Italian-developed IBEX balloon spectrometer is its ability to measure all accessible HBr spectroscopic emission lines at the highest spectral resolution. It is estimated that a measurement using today's upgraded balloon spectrometer and new detector technology will provide, conservatively, a four-fold improvement in HBr sensitivity, compared to the 1979 measurements. This study is currently under way with a flight window scheduled for May 1 - 7, 1993.

MBGC will fund this project at $135,000 and it should be completed in one year.

2. Dr. Darin W. Toohey of the University of California, Irvine, will investigate the concentration of BrO in the stratosphere. He will examine in detail all of the *in situ* BrO measurements obtained to date from the ER-2

aircraft. To accomplish this objective, uncertainties in the calibration standards will first be reduced. Because BrO is unstable and cannot be collected for analysis in a laboratory at a later time, past data was detected in real time using the technique of resonance fluorescence. Thus, the data obtained in flight are stored in archival form, and can be reevaluated without adding any error. With more accurate laboratory pre- and post-flight calibrations, the measurements obtained directly in the atmosphere will also be improved substantially. Therefore, a thorough analysis of all the calibration data combined with the recent improvements to the ClO calibrations will allow Dr. Toohey to report BrO with an absolute accuracy of about 20 - 25%. This reduction in uncertainties will allow for more detailed and meaningful interpretations of the chemistry of bromine in the lower stratosphere.

MBGC will fund this project at $84,338 and will take two years to complete.

3. In his second project, Dr. Toohey will design and build an ultra-high vacuum facility to produce high quality bromine resonance lamps. These lamps, when substituted into an instrument to measure reactive chlorine (being built at UCI), should extend the capability to measure BrO with high precision above 20 km. These measurements, along with simultaneous measurements of HBr, will improve the understanding of bromine photochemistry and constrain models that are used to predict the impact of inorganic bromine on ozone in the lower stratosphere.

   MBGC will fund this project at $88,930 and it will take two years to complete.

C. SOURCES AND SINKS

The sources and sinks for methyl bromide are very poorly understood. This makes it difficult to assess the role of natural and anthropogenic methyl bromide in the global atmospheric budget. Complicating this situation is the lack of good tropospheric measurements of methyl bromide, inadequate calibration standards, and limited ocean data. Uncertainties in these factors need

to be reduced to get a better understanding of methyl bromide's true tropospheric lifetime.

Currently, calculations for methyl bromide's lifetime are based solely on the reaction of methyl bromide with the OH radical in the troposphere. Indirect evidence suggests that other removal processes could play a role in the removal of methyl bromide from the troposphere. If other removal processes exist this will result in a lowering of the atmospheric lifetime for methyl bromide.

There are three possible sinks for methyl bromide which need to be investigated. These are vegetation, soil, and the ocean. Although the magnitude of these potential sinks is unknown, it has been calculated that the impact of ocean uptake could reduce methyl bromide's total lifetime to 1.3 years (Sze et al, 1992). If this ocean sink is included in the ODP calculation for methyl bromide, then the range of ODP values would be 0.15 - 0.53. Removal by soil and vegetation could reduce this ODP even more.

Four studies are being funded by the Methyl Bromide Global Coalition. One of these will look at the soil and vegetation as a sink for methyl bromide, two will look at the ocean as a source and/or sink of methyl bromide, and one will generate atmospheric measurement data for methyl bromide using better calibration standards.

1. Dr. Kolb of Aerodyne Research and Dr. Bob Harriss of the University of New Hampshire propose to conduct a two year investigation of the deposition of methyl bromide to soil and vegetation. Their study will determine the uptake of methyl bromide by soils due to the cumulative processes of dissolution into soil water, absorption to soil organic matter, and microbial degradation. The uptake by plant leaf surfaces will also be investigated. The effect of simulated near-ultraviolet and visible sunlight on these processes will also be determined. Coastal New Hampshire and Massachusetts soils exhibiting a wide gradient in organic matter content will be used in both laboratory batch (static) and field flow-through chamber (dynamic) studies. They will also evaluate

the effects of temperature, soil moisture and organic matter content on the gross rates of aerobic uptake of atmospheric methyl bromide. The data obtained in this project will be used to develop apparent reaction rate constants for each soil type and treatment. Such data and a correlating model are crucial for proper evaluation of the lifetime of methyl bromide in the Earth's atmosphere.

MBGC will fund this project at $389,315 and it will be completed in two years from initiation.

2. Dr. James Butler of the National Oceanic and Atmospheric Administration proposes to measure methyl bromide with shipborad instrumentation in the surface ocean, atmosphere, and at depth across an oceanic transect that crosses both cold and warm water and both productive and unproductive regions of the ocean. In this manner, he should be able to constrain the direction and magnitude of the air-sea flux of methyl bromide under a range of common oceanic conditions. From these results, he will be

able to assess with much more confidence the role of the ocean in regulating the concentrations of atmospheric methyl bromide, as well as more accurately define the global budget of methyl bromide.

MBGC will fund this project at $307,000 and it will take two years to complete from initiation.

3. Dr. Ray Weiss of the Scripps Institution of Oceanography, University of California, San Diego, proposes to conduct research in three areas: the development of absolute calibration standards; atmospheric measurements of methyl bromide; and ocean measurements of methyl bromide. In the development of the calibration standards, Dr. Weiss proposes to carry out absolute gravimetric methyl bromide calibrations at ambient concentration levels using the same equipment and techniques as for his AGAGE work. Such calibrations are critical to determining the atmospheric budget and quantitatively relating the tropospheric

residence time to the natural and anthropogenic fluxes.

In his atmospheric sampling program, Dr. Weiss plans to set up a time series of flask measurements at Scripps' pier in La Jolla, as well as participate in the AGAGE program at sites such as Cape Grim, Tasmania. Measurements will also be made of methyl bromide concentration in ocean waters.

MBGC will fund this project at $113,000 and it will be completed in a two year period.

D. EMISSION REDUCTION

BACKGROUND: It has been estimated that approximately 50% of man-made methyl bromide gets emitted into the troposphere. Because of the potential for man-made methyl bromide to effect the ozone layer, it is prudent for the users of methyl bromide to develop application methods which result in the lowest emission rates possible, as well as quantify those emission rates.

An international program will develop data on emissions from soil applications. Procedures will be developed to reduce emissions while maintaining the efficacious use of the product.

1. Currently, a Japanese project on soil emission reduction has been funded and five European projects on soil emission reduction are being developed.

   MBGC has set aside $300,000 to cover all of these projects. These studies will be completed in one year from initiation.

SUMMARY

The Methyl Bromide Global Coalition will invest approximately $1.9 million on research, modeling, and program administration to enable the international scientific community to reduce the uncertainties associated with anthropogenic methyl bromide's effect on stratospheric ozone. This research program is achievable in two years and involves the world's leading atmospheric scientists. Results of this research will be presented at workshops and scientists are encouraged to publish their findings in peer reviewed Journals.

In addition NASA is funding a similar series of studies. NASA's methyl bromide research program will cost $0.9 million and all of their results should be available in the next 2-3 years. The USDA is funding research on methyl bromide emissions and emission reduction from soil fumigation use. This research will cost $ 500,000 per year for the next three years.

MBGC, NASA, and USDA are working closely in an attempt to get the maximum benefit from their programs in the shortest time possible.