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Methyl Bromide

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file - methyl bromide.

POSITION ON METHYL BROMIDE

The parties to the Montreal Protocol have agreed that methyl bromide should be listed with an ODP of 0.7, production and consumption should be capped in 1995 at 1991 levels, that a two-year study should be undertaken to clarify uncertainties with regard to the setting of an appropriate ODP level, and that the whole issue should be reassessed in 1995. The failure of the parties to take a more definitive position reflects substantial concern over the data available to establish an ODP level.

The Clean Air Act requires EPA to be consistent with the Montreal Protocol. We believe this can be accomplished while avoiding major disruptions to U.S. agricultural production and trade and allowing critical research for alternatives to proceed.

We would support:

1. Listing methyl bromide as a Class II substance,
2. Assigning an ODP (ozone-depleting potential) range of 0.1 to 1.3, with designation of 0.7 as a best estimate given current data (assignment of a wide range for the ODP accurately reflects the current scientific uncertainty),
3. Place a cap on production and consumption in 1995 at 1991 levels,
4. Conduct a two-year study with re-evaluation of the data in 1995, and
5. Publish this proposal separately from the refrigerant ozone-depleting chemicals (methyl bromide is an entirely different type of chemical).

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By initially designating methyl bromide as a Class II substance, and if the study shows it to be unequivocally a Class I substance, the EPA can easily reclassify it. The reverse is not true.

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The Class II designation would allow a more reasonable timeframe to develop alternatives to methyl bromide and to gain their acceptance by trading partners.

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Current Understanding of the Ozone Depleting Potential of Methyl Bromide

Background

Methyl bromide (CH_3Br) is a relatively short-lived, ozone-depleting gas with both natural and anthropogenic origins. On a per-unit basis, bromine compounds are known to have a much larger impact on the ozone-layer depletion than do chlorine compounds, but the details of stratospheric bromine chemistry are not as well understood as the chlorine counterparts. The Ozone Depletion Potentials (ODPs) of compounds with shorter atmospheric residence times (e.g., the HCFCs and methyl bromide) are more difficult to calculate accurately than those of the longer-lived compounds (e.g., the CFCs and halons).

Based on the current state of knowledge of the atmospheric science of methyl bromide, the calculated long-term steady-state ODP of CH_3Br is 0.65, using the current values for the rates of removal via reaction with the hydroxyl radical (OH), which yield a CH_3Br atmospheric lifetime of 1.7 years. The shorter-timescale ODP of CH_3Br , say for the next 20 years when ozone depletion will be at its maximum, is much larger than 0.65.

Approximately 25% of atmospheric CH_3Br is human-made because: (i) the measured atmospheric concentrations of 9 - 13 pptv, global atmospheric distribution (specifically, the ratio of the CH_3Br concentrations between the northern and southern hemispheres of 1.3) and the atmospheric lifetime of ~2 years show that 80-120 thousand tonnes of CH_3Br is emitted into the troposphere per year and (ii) anthropogenic emissions are about 30 thousand tonnes per year from industry figures. This suggests that anthropogenic emissions of CH_3Br used for fumigation applications could have accounted for about one-tenth to one-twentieth of the current observed global ozone loss of 4 - 6% and could grow to about one-sixth of the predicted ozone loss by the year 2000 if the CH_3Br emissions continue to increase at the present rate of 5 - 6% per year.

Uncertainties in the ODP

Atmospheric lifetime. Reactive uptake (hydrolysis) of CH_3Br by oceans and soils is assumed to be zero in the above calculations. If they were to prove to be efficient, they could lower the atmospheric lifetime of CH_3Br . Lowering the atmospheric lifetime has two effects: (i) it lowers the ODP of CH_3Br and (ii) it changes the human contribution to the CH_3Br present in the atmosphere. If these uptake processes were to reduce the atmospheric lifetime to 0.5 year, the steady-state ODP of CH_3Br would be less than the Clean Air Act Amendments threshold of 0.2. However, such a short lifetime would, in turn, require a much larger human input to explain the observed atmospheric concentrations and the north/south ratio. There is no experimental

evidence to suggest that oceans are a large enough sink to reduce the lifetime of CH₃Br to less than 1 year.

The HO₂ + BrO reaction. The reaction of HO₂ with BrO, which is an important factor in the catalytic destruction of O₃, has been deemed recently to be faster than previously believed when the ODP of 0.65 was calculated. This faster rate increases the steady-state ODP of CH₃Br to ~1.2, assuming an atmospheric lifetime is 1.7 years, unless the products of this reaction include HBr + O₃. However, there is no experimental evidence for these products. Even the analogous HO₂ + ClO reaction is not known to give HCl + O₃. The complex rearrangements required to give HBr + O₃ make these products unlikely. In the unlikely event that these products are produced 10% of the time, the ODP of CH₃Br could be as low as 0.25.

Summary

The newly adopted faster rate for the reaction HO₂ + BrO indicates that ODP of CH₃Br is larger than 0.65. For the ODP of CH₃Br to be below 0.2, the lifetime of CH₃Br would have to be less than one year, which appears unlikely, and 10% of the HO₂ + BrO reaction would have to yield HBr, which appears to be even more unlikely. In the likely event that the reaction of HO₂ with BrO does not give HBr, the lifetime of CH₃Br has to be less than 0.5 year for its ODP to be less than 0.2. Based on the best available data, it seems unlikely that ocean hydrolysis or soil uptake of CH₃Br would reduce its lifetime to a value less than one year. If it did, the human contribution to the atmospheric abundance would have to be much larger than currently thought.

Ravishankara, Solomon, and Albritton: 11 February 1993

Based on "Methyl Bromide: Its Atmospheric Science, Technology, and Economics" (UNEP, June 1992) and "Chemical Kinetics and Photochemical Data For Use in Stratospheric Modeling. Evaluation No. 10" (JPL, August 1992).

— 2/9/93

Katie McGinty

FYI per our conversation.

Martha Foley
Lit. 6190

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Methyl
Bromide

THE OFFICE OF THE SECRETARY
WASHINGTON
20250-0100

February 5, 1993

Honorable Leon Panetta
Director of the Office of Management and Budget
Executive Office of the President
252 Old Executive Office Building
Washington, D.C. 20503

Dear Leon:

I submit to you the following comments regarding the EPA's proposed rulemaking on Methyl Bromide.

Assignment of 0.7 as the ODP for Methyl Bromide

The calculation of 0.7 as the ODP for methyl bromide assumes that the OH radical is the only significant tropospheric loss mechanism. In fact, the UNEP Science Assessment Report clearly identifies two surface removal processes, deposition of methyl bromide on soil or vegetation and the uptake by surface waters of the ocean. Methyl bromide being a polar molecule and a strong methylating agent should adsorb on the surfaces of soils and vegetation. The report states that quantifying the significance of dry deposition would improve our understanding of methyl bromide sinks. The removal processes of methyl bromide in surface waters of the oceans could be significant and "the magnitude of this sink would depend upon the rate of air-sea exchange, on the solubility of methyl bromide in ocean waters, and its chemical degradation by OH⁻ and Cl⁻. The report also states that ion exchange with Cl⁻ to form CH₃Cl is an efficient aquatic sink for CH₃Br. Models that yield ocean removal lifetime for ¹⁴CO₂ of 7.3 years (in good agreement with observations) would imply a lifetime for methyl bromide of 3.3 years considering this process. Therefore, ocean surface removal could be significant, but remains to be quantified.

The UNEP Science Assessment identified two high priority near term research needs that would enable a significant improvement in understanding methyl bromide sinks and their effect on the ODP. These research priorities are as follows:

- Conduct measurements of both methyl bromide and methyl chloride concentrations in surface waters, as well as in air immediately above, to explore how the CH₃Cl data set can provide insight into the oceanic source or sink for methyl bromide.
- Carry out field measurements with gradient and enclosure methods of the

atmospheric deposition of methyl bromide to soils and vegetation to establish the possible significance of these sinks.

The UNEP Assessment report identifies these additional sinks as highly probable and potentially significant. Therefore, it is premature to assume unequivocally that the OH radical is the only significant removal source. Further it cannot be assumed that if these other sinks are significant, the resulting decrease in the ODP would not be significant enough to lower the ODP to less than 0.2 (Table 1).

USDA disagrees with EPA's discounting the possibility for the formation of HBr. EPA has placed emphasis on new "laboratory" data indicating a faster rate of HOBr formation (via $\text{BrO} + \text{HO}_2$) resulting in a somewhat larger ODP. These studies were conducted under laboratory conditions and would not be representative of the heterogeneous chemistry which occurs in the atmosphere. The Science Assessment Report points out very clearly that the partitioning (for the formation of the species HOBr, HBr, BrCl, BrONO₂) is quantitatively dependent on the rates of the various photochemical reactions and hence has a marked dependence on altitude, latitude, and seasons, as well as on the abundances of species such as NO₂, HO₂, OH, etc. The occurrence of a pathway for producing HBr would appreciably lower the catalytic efficiency of the heterogenous cycle and of stratospheric bromide in general.

The assessment report clearly points out that an additional quantitative investigation of the rate, and production and distribution of the $\text{BrO} + \text{HO}_2$ reaction under stratospheric conditions of temperature and pressure would help to evaluate this reaction. In addition, studies of the formation of HBr by other reactions such as $\text{BrO} + \text{HO}$ and $\text{Br} + \text{HO}_2$ would help to improve the understanding of bromine partitioning in the stratosphere.

Some preliminary data show that if these additional sinks are taken into consideration and if one assumes a faster removal rate by $\text{BrO} + \text{HO}_2 \rightarrow \text{HBr}$, the ODP would decrease significantly below 0.2 (Table 1). There is no quantitative evidence for the determination of HBr, but there is laboratory evidence for appreciable HCl formation from an analogous reaction, $\text{HO}_2 + \text{ClO}$ [Kuo, Y.P., S.S. Ju, and Y.P. Lee (1987) J.Chin.Chem.Soc., 34, 161-168].

Therefore, EPA is incorrect in disregarding the significance of the partitioning rates for possible formation of HBr. The importance of the formation of HBr is that it reduces the catalytic efficiency of bromine.

Anthropogenic vs. Natural sources for Methyl Bromide

EPA has cited a number of studies which attempt to estimate the amount of methyl bromide emitted to the atmosphere as a result of soil fumigation use. There were wide variations in the percent of methyl bromide emitted ranging from as low as 20 percent to a high value of 87 percent. Levels of emissions vary with injection depth, soil texture, organic and moisture content, application rates, and the time the exposed areas remain tarped. We do not disagree that large portions of the applied methyl bromide may be emitted to the atmosphere, but since USDA was informed about the potential impact of methyl bromide on the ozone, we have been looking at ways to significantly reduce methyl bromide emissions from soil injections,

commodity treatments, and quarantine. We have convened a group of approximately 35 agricultural experts from government, academia, and industry and are developing a comprehensive research plan to address levels of methyl bromide emissions, e.g., new or improved technologies, methods of application, application rates, and permeability of plastic tarps. We are convinced that significant reduction in levels of emissions can be achieved.

We support the recommendations in the UNEP Science Assessment report to "[C]arry out field and modeling studies to quantify better the emission factors for the major application e.g., preplanting fumigation, and to identify major controlling factors which would improve the estimates of the contributions of human activities and aid the design of new application techniques." The research projects which we are developing are consistent with the UNEP proposal. The final analysis should provide the information which policy makers need for scientifically sound decisionmaking.

USDA also supports the UNEP report's recommendation "to investigate other possible sources [for methyl bromide], for example, those from the transportation sector, inadvertent industrial production, and biomass burning to assess the completeness of emission inventory." At the September 21-23, 1992 USDA Methyl Bromide Research Workshop, an EPA representative stated that the manufacturing of polyethylene is another source for methyl bromide. In the proposed EPA's draft notice of Proposed Rulemaking other potential sources for methyl bromide are not discussed.

It is well documented in the literature that the oceans are considered to be the major natural source for methyl bromide. As much as 95 percent of the methyl bromide in the atmosphere comes from the oceans and other natural sources. USDA strongly supports the recommendations of UNEP Science Assessment Report's recommendation to quantify the natural sources of methyl bromide.

In EPA's draft document for proposed rulemaking it appears that the only significant methyl bromide emissions come from anthropogenic sources; natural sources and the need to differentiate from man-made sources have not been addressed. Since natural sources are the major contributors of atmospheric methyl bromide, we question if reduction of man-made sources would have a significant impact on ozone depletion, particularly since most of the data regarding man-made contributions are "assumed, estimated, extrapolated" or even "guessed." It appears that a more scientific approach would be to focus on studies that would provide the scientific credibility needed for good decisionmaking.

Alternatives for Methyl Bromide

On several occasions EPA has quoted a statement taken from the UNEP Technology and Economic Assessment Workshop Report "that a significant fraction (30-90 percent) of methyl bromide used for soil fumigation could be replaced by chemical substitutes by the year 2000." The "30-90 percent" was determined by hand vote taken at the end of the workshop when many who participated in the soil fumigation group had already left. The statement is grossly misleading, and EPA should refrain from using numbers which cannot be substantiated.

USDA, working with the methyl bromide industry, academia, agricultural applicators, manufacturers of alternative chemicals, and quarantine regulators, has assessed available chemicals for potential alternatives as well as identified uses where research is needed for new chemical development. As indicated in the UNEP Technology and Economic Assessment Report and confirmed at the September 21-23, 1992 USDA research planning workshop, there is no single chemical that will equivalently replace the broad spectrum activity of methyl bromide for soil fumigation. There are some chemicals which will afford some level of pest control, albeit reduced, and with a narrower pest activity range. Further, no new fumigants for quarantine substitutes have been identified in the past 15 years, and none are likely in the foreseeable future. Many of the compounds previously identified have been withdrawn from use due to toxicological, residue or environmental concerns or other constraints under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA).

Biologically based pest management including host resistance, cultural practices and biological control may provide some alternative control for soil fumigation in specific crop and pest situations. However, such resistance may be short-term as pathogens have a tendency to overcome biologically engineered resistance. Additionally, biologically based pest management is specific to each geographic area or region, with specific management systems requirements that will necessitate long term research programs throughout the U.S.

Non-chemical alternatives for quarantine will require a combination of treatments or a systems approach. It is unlikely that these alternatives will be capable of handling the import or export volumes or meet the time elements to coincide with the short shelf-life of most perishable commodities. Too, these alternatives are labor intensive and therefore costs will be increased dramatically as compared to the cost for methyl bromide. For the preponderance of commodities treated in quarantine for which no alternative is feasible, irradiation may be required. Logistically this alternative is extremely difficult, not just from the standpoint of consumer acceptance, but also from a legal perspective. For example, irradiation is illegal in some U.S. states as well as with a number of our trading partners, e.g., Japan, New Zealand, and Colombia. There is no assurance that this situation will change.

We have met with the manufacturers of Dazomet and Telone. While Dazomet is used in a number of countries as a soil fumigant on edible crops, its use in the U.S. is limited to non-food items only. The manufacturer plans to register Dazomet in the U.S. for limited number of food crops: strawberries, tomatoes, peppers, and broccoli. The studies to generate the data to support these four registrations are in their very early stages. Registration is probably 3-5 years away or even longer. No expansion of the registration to cover additional food crops is anticipated.

Telone (Telone I and Telone II) is under EPA review. At this juncture, it is unclear how many food uses will be retained in the reregistration process. Also, its not known if it will be reinstated in California where its uses are currently suspended.

Vorlex is another soil fumigant which the manufacturer has chosen not to reregister, and it is unlikely that it will be picked up by another registrant.

Therefore, of the few chemicals which remain as potential alternatives for soil treatments, the EPA reregistration requirements under FIFRA will eliminate some altogether and certain uses of those remaining. The continued Congressional oversights and stiffening requirements of FIFRA have forced the chemical industry to shy away from pesticide production and exploration. The proposed actions under the CAA exacerbates this situation. Under the current situation, it is highly unlikely that a new chemical will be developed to replace methyl bromide or registrations expanded for the few chemicals that exist. The continued decline in the availability of agricultural chemicals has been occurring over the past ten years; more severely, since the 1988 FIFRA amendments.

The Montreal Protocol and the U.S. Clean Air Act

At the April 5-17, 1992 meeting of the Open-Ended Working Group to the Parties of the Montreal Protocol, the U.S. (EPA) recommended that methyl bromide be added to the list of international substances that deplete the ozone and be totally phased out by the year 2000. USDA was a member of this delegation and had related to the delegation that we were not comfortable with this recommendation for reasons cited above. The U.S. recommendation caught most delegations by surprise.

Since other delegates did not have a pre-cleared country position, they were unable to respond to the U.S. proposal. However, at the July 5-18, 1992 meeting, it became unequivocally clear that the U.S. position had not been well-received; no support was given to the U.S. Most delegations, while raising concern over the possibility of methyl bromide depleting the ozone, recognized that the data from the UNEP Science Assessment report was far from being complete. In view of the importance of this chemical to agricultural production and trade, they recommended a more cautious approach. A number of alternate proposals were tabled, none of which went as far as the U.S. It is most unlikely that there will be any support for the U.S.(EPA) position.

Other countries are basing their decisions on the same data base (the UNEP Science Assessment Report) as the U.S., and therefore it concerns USDA that we are placing ourselves in a unfavorable position with the rest of the world. USDA strongly recommends that the U.S.(EPA) withdraw its proposal and join the rest of the world in attempting to resolve some of the uncertainties with the data as delineated in the UNEP Science Assessment Report. Once these data have been generated, the issue can be reevaluated and action taken accordingly.

The draft document states that "The Agency believes that while a 2000 phaseout date is clearly mandated by the Clean Air Act (CAA), that period may not provide adequate lead time for the development and approval of substitutes for all of the current uses of methyl bromide. The Agency believes that an essential use provision which allows the continued production of this compound after the year 2000 would be highly desirable." The document refers to the Montreal Protocol which was amended in 1990 to include an essential provision for the halons and is currently being discussed to include all compounds including methyl bromide if it is added to the Protocol.

EPA has stated on numerous occasions that if the expanded essential use provision for the Montreal Protocol is passed, this will give them the leverage to go to Congress to get the CAA amended consistent with the Protocol. Further, EPA has supported the essential use provisions to the Montreal Protocol although knowing that the U.S. has no statutory provisions to support the concept. Supporting a binding amendment in an international convention without appropriate legislation to implement that amendment domestically appears to be "contrary" to the spirit of international conventions. If the Protocol is amended and the CAA is not, the U.S. industry and consumers will be at a disadvantage with the rest of the world. Also, this process appears to be a "back door" approach to Congress to get the CAA amended. In a recent letter from Congressman Dingell, he stated "[A]s a matter of policy, I think it wrong for anyone in the Administration to suggest or hold out hope informally, or otherwise, that at some future time there may be amendments to the CAA. I think this is wrong in the context of potential rulemaking and international negotiations...I assume that such a suggestion is not the official position of the Administration or the EPA and that EPA and the Administration will not base its actions on the "hope" of such a potential amendment."

Sincerely,


MIKE ESPY
Secretary