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Minimizing methyl bromide emissions from soil fumigation

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Abstract. There is great controversy concerning the need to phase out methyl bromide (MeBr) to protect stratospheric ozone. Unlike chlorinated hydrocarbons, MeBr occurs naturally in the atmosphere making it difficult to differentiate the threat to stratospheric ozone depletion from anthropogenic use of MeBr compared to natural sources. New technology has been developed which could nearly eliminate MeBr emissions from soil fumigation, bringing into question the need for a phase out. A field experiment demonstrated that virtually impermeable films (VIF) reduced MeBr emissions to near-zero levels. When compared to soil fumigation using conventional high-density polyethylene film (HDPE), the total global MeBr emission could be reduced from 32 Gg/yr to less than 1 Gg/yr, if VIF were required. In addition, reduced application rates are possible since using VIF reduces wasteful leakage and increases pest-control efficiency. With such low emission rates, and considering the large uncertainty in global estimates of MeBr, it seems that the phase-out of MeBr as a soil fumigant is unjustified.

Introduction

Methyl bromide (CH_3Br, bromomethane, MeBr) has been implicated as a chemical that depletes stratospheric ozone [*Wofsy et al.*, 1975] and under the provisions of the U.S. Clean Air Act, will be phased out in the United States by the year 2001. The international community has also voiced great concerns. The countries participating in the Montreal Protocol agreed that use of MeBr will be eliminated by industrial countries by the year 2010. In addition, they agreed to a 25% reduction in production by the year 2001 and a 50% reduction by 2005. It was also decided that production of MeBr in developing countries would be frozen in 2002 and MeBr use would be eliminated later in the century. This has prompted scientists to develop a global budget of sources and sinks of ozone-depleting, halogenated gases, including MeBr [*Singh and Kanakidou*, 1993; *Khalil et al.*, 1993; *Butler*, 1995].

MeBr has been used for decades to control soil-borne pests such as nematodes, weeds and fungi before planting fruits and vegetables in many parts of the world. An economic assessment by the USDA, National Agricultural Pesticide Impact Assessment Program [*NAPIAP*, 1993] found that the negative economic impact caused by a MeBr phase-out will be especially severe on the agricultural community. For example, it has been estimated that at least $1.5 billion in annual lost production in the United States [*NAPIAP*, 1993; *Ferguson and Padula*, 1994] will occur if MeBr use is restricted.

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To understand the role of soil fumigation in supplying the atmosphere with anthropogenic MeBr, several field-scale experiments have been conducted to measure MeBr losses after soil fumigation [*Yagi et al.*, 1993, 1995; *Majewski et al.*, 1995; *Yates et al.*, 1996a, b, c; *Williams et al.*, 1997; *Wang et al.*, 1997a, b]. These studies have shown that from 27-87% of applied MeBr may be lost to the atmosphere after shallow injection at 25-30 cm depth and completely covering the soil surface with high-density polyethylene plastic (HDPE). The large emission losses are caused primarily by the ineffectiveness of HDPE to trap MeBr gases [*Yates et al.*, 1997]. Standard HDPE has a permeability factor (equivalent to the volatilization rate when a 1 mg/L concentration gradient occurs across the film) of approximately 7.4 mg/m^2/h and is widely used in soil fumigation because of its low cost and physical and mechanical characteristics which make it easy to use in farming operations.

Using the reported total emission measurements, the cumulative frequency distribution can be plotted for the total MeBr emission (%) after shallow injection under HDPE plastic. This is shown in Figure 1. The high variability in the total measured emission loss may be attributed to a variety of factors including: differences in soil and environmental conditions that are indigenous to the location where an experiment is conducted, principally the ambient temperature during fumigation and local variations in soil degradation; and differences in the experimental methods used to measure the emission rate.

New plastic films have been developed that are nearly impermeable to MeBr. For example, $Hytibar^{TM}$ film, (Klerk's Plastic, Belgium) is manufactured by incorporating a barrier polymer, ethylene vinyl alcohol, into the center of a polyethylene film. Tests in the laboratory have shown that this new plastic is from 75 to 200 times less permeable to MeBr than the conventional plastic films [*Yates et al.*, 1997; *Wang et al.*, 1998]. Since $Hytibar^{TM}$ is predominately polyethylene, it also has physical and mechanical properties that are similar to the conventional plastic films and should be suitable for field use, although further testing is needed under the harsh conditions that occur in large agricultural fields.

The soil's ability to degrade MeBr is another important factor affecting the ultimate emission rate. However, with reported half-lives in soil ranging from 5 to 28 days [*Gan et*

Table 1. MeBr Emission Losses [*Wang et al.*, 1997a]

Cover Period (days)	Total Volatile Loss After, (%)			Mass Balance (%)
	5 d	10 d	15 d	
HDPE[a]				
15	63.6	66.9	66.9	108.0
10	49.3	54.8	56.4	86.7
5	61.9	67.7	68.0	95.8
VIF[b]				
15	1.5	1.8	1.9	98.9
10	1.0	1.4	1.8	102.0
5	1.9	33.9	36.2	105.2
VIF[c]				
15	0.9	1.0	1.1	94.9
10	2.6	2.9	2.9	98.3
5	10.4	38.5	38.8	100.0

[a]Application rate: 280 kg/ha
[b]Application rate: 210 kg/ha
[c]Application rate: 140 kg/ha

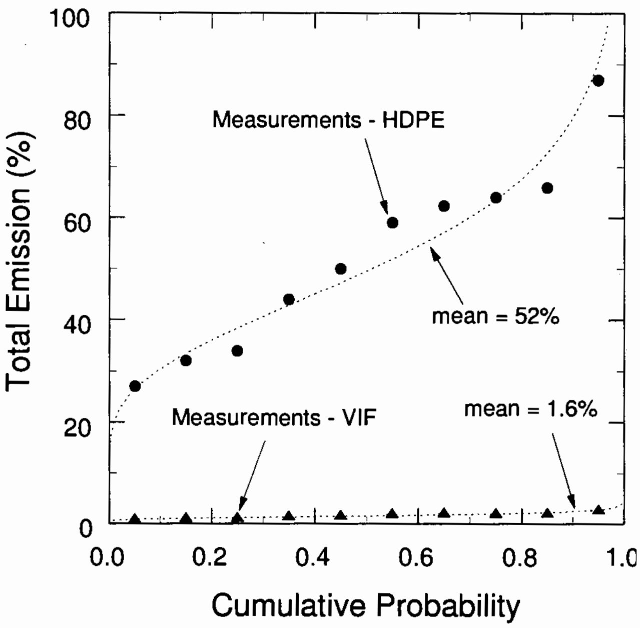

Figure 1. Cumulative probability distribution for total MeBr emission into the atmosphere. Solid circles are from field-scale measurements, open squares are predicted values for VIF and lines are theoretical log-normal probability distributions with the indicated mean values. The coefficient of variation (e.g., σ/μ) for both measurements and predictions is 0.34.

al., 1994], soil degradation will not be an important factor unless the MeBr is completely contained in soil for relatively long periods. Traditional HDPE is too permeable to provide necessary levels of containment.

Demonstrating Reduced Emissions

In the U.S., MeBr is commonly injected 25-30 cm deep into soil, at a rate of approximately 280 kg/ha, and the field is covered with plastic for 2 to 5 days. To determine if MeBr emissions can be effectively eliminated by using VIF, a field study was conducted in which MeBr emissions from field plots were measured [*Wang et al.*, 1997a]. Three scenarios were tested: (a) common fumigation practices using HDPE film and an application rate of 280 kg/ha (100% dosage); (b) VIF and a 210 kg/ha rate (75% of the standard rate); and (c) VIF and a 140 kg/ha rate (50% of the standard rate). When HDPE plastic was used to cover the field, the total emission losses were between 56 and 68% of the applied chemical (Table 1).

This range is very consistent with other experiments conducted in this area of California [*Yates et al.*, 1996a, b, c; *Wang et al.*, 1997b]. When VIF was used to seal the surface for 5 days, total emissions were reduced to 36-39%. Most of this loss occurred immediately after the plastic was removed from the soil surface as the MeBr gas trapped under the plastic and in the near-surface soil was released. If the VIF remained on the field for 10 to 15 days, the total losses were less than 4%.

Note that for the VIF plots, the same fractional percentage of total volatilization occurs regardless of the initial application rate. For many of the plots covered with VIF for 10-15 days, the ratio of the total emission from a VIF plot to the average of the HDPE plots is of the same order of magnitude as the ratio of the permeability of VIF to HDPE. This suggests that the experiment could be used to extrapolate measured total emissions from other experiments that used HDPE to predict what might occur if VIFs were used.

Using the distribution of agricultural MeBr emissions shown in Figure 1, a rough assessment can be made of the effect of using VIF's on the global MeBr balance. This can be accomplished by scaling the recent measurements using the data in Table 1. The extrapolation proceeds by determining the average total emissions from experiments conducted in the Riverside, CA area including a 1993 experiment where the total emissions were reported in the range 61 - 70%, a 1995 experiment with a total emission of 59% and the results from Table 1. This yields an average of 64% for HDPE. Next, the total emissions from the plots covered with VIF for 10 and 15 d (Table 1) is estimated to be 1.9%. An extrapolated emission rate can be obtained by multiplying each total emission rate in Figure 1 by the ratio: (avg. VIF)/(avg. HDPE) or 1/33 or 0.03. The potential mean emission rate from soil fumigation using VIF is also shown in Figure 1 and is 1.6 %. This represents a 33-times decrease in the mean total loss and should be expected given that this plastic has a permeability 75 to 200 times less than HDPE.

To test this further, MeBr diffusion and degradation in soils was simulated to investigate how changes in the surface resistance caused by the presence and removal of the plastic film affect volatilization. Using data from *Wang et al. [1997c]* to parameterize the model (injection depth, 30 cm; soil diffusion, 800 cm^2/day; soil degradation half-life, 6 days; mass transfer coefficients, respectively, for HDPE, 54 cm/day; *Hytibar*^{TM}, 0.27 cm/day and bare soil, ∞ cm/day), the total emission when the soil is covered with HDPE for 5 days was predicted to be 60%. When VIF is used for 5 days, predicted loss is approximately 32%; these

Table 2. Current and Projected Global MeBr Budget. Adapted from *Yvon-Lewis and Butler [1997]*

Sinks	Global Degradation (Gg/yr)	Sources	Current Emission Estimate (Gg/yr)	Potential Emission Estimate (Gg/yr)	Potential Contribution to Global (%)
Oceans	77	Oceans	56	56	57
OH and h_ν	86	Soil Fumigation	32	1	1
Soils	43	Other Fumigation	14	14	14
Plants	unknown	Gasoline	1-15	1-15	8
		Biomass Burning	20	20	20
Totals	>206	Totals	130[a]	99	100

[a]Used 8 Gg/yr for gasoline

values are close to those reported in Table 1 (e.g., 56-68% and 36-39%). If the VIF cover period is increased to 15 days, the predicted loss is only 7%. The difference between the 7% prediction and the 1.9% measured loss from the 15d VIF plots is well within the deviation in the mass balances. Thus, the model provides additional support for the results from the field experiment.

Implications for Regulating MeBr Use

The results from this study have important implications for the global MeBr budget. Currently, agricultural emissions from soil fumigation contribute about 32 Gg/yr (or 25%) to the global MeBr budget [*Yvon-Lewis and Butler*, 1997]. If all fumigation used VIF and followed the results in Figure 1, the volatile emissions would be reduced by a factor of 33, suggesting that the total MeBr input from soil fumigation would be reduced from approximately 32 to approximately 1 Gg/yr, or 1% of the total. This value is lower than the uncertainty of every other number shown in Table 2.

Another factor that should be considered is that the application rate can be reduced when VIFs are used. When HDPE is used, large quantities of MeBr are needed to compensate for the leakage into the atmosphere. Using VIFs, there is less leakage and, as a result, less chemical is needed to achieve the same level of pest control. This was demonstrated in the experiment of *Wang et al. [1997a]* where application rates that were 25% less than standard were shown to provide a similar level of pest control compared to the HDPE case. Using reduced application rates would lower the global contribution from soil fumigation to even less than 1%.

Conclusions

The current paradigm of eliminating any chemical which has the potential to pose an environmental problem is sufficiently simple to appeal to many people. The problem is that, once eliminated, it seems impossible to "phase-in" a chemical if new technology produces methodology that is environmentally benign, or future research demonstrates that the chemical was never a serious problem. In a sense, the current paradigm inhibits technological advance, in this case the exploration for environmentally-benign solutions. Once the phase-out call has been made, all efforts are directed toward the search for alternatives, many of which may be more environmentally damaging in their own fashion.

A new paradigm is needed where it is recognized that every chemical can be a "problem", in some sense, and provides incentives to develop technology to minimize these characteristics before they become environmental or public-health problems. If the appropriate technology is unavailable, rather than banning the use of a chemical, it would be better to formulate the regulation so that the chemical cannot be used until the undesirable characteristic(s) can be appropriately controlled.

For example, if the Clean Air Act was written in such a way that chemicals that deplete stratospheric ozone (i.e., ozone depletion potential >0.2) could not be used unless the total emissions would be less than a specified mass per year (e.g., 2 Gg/yr), MeBr would have been effectively banned for an indefinite period since the current total emissions from soil fumigation far exceed this value. This would also have started a research effort to reduce emissions which, after the introduction of VIF's, would provide a means to lift the ban.

As the target date to eliminate MeBr nears, there are serious questions whether the phase-out will have any significant effect on stratospheric ozone levels [*Honaganahalli and Seiber*, 1997]. Only recently has it been recognized that indigenous plants produce MeBr [*Gan et al.*, 1998]; and it has been suggested that the ocean will act as a buffer [*Butler*, 1994], contributing MeBr to the atmosphere to offset any reduction in anthropogenic emission. If this happens, then the agricultural community and society lose, since the ban will only cause the loss of an effective broad-spectrum soil sterilant and do little to stop ozone depletion. This will make it much more difficult for farmers to provide an adequate food supply in the U.S. and elsewhere in the world. In fact, the Montreal Protocol does not propose an elimination of MeBr far into the next century, only a world-wide reduction in anthropogenic emissions. Unfortunately, the burden of this reduction will be forced on the industrialized nations, those nations which can develop technology to significantly reduce emissions. The same goal can be achieved using VIFs producing greater emission reduction without negative side effects on the Nation's economy and food supply. There is no debate that stratospheric ozone must be protected, but, the means of protection remains debatable.

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