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Laboratory-Scale Measurements and Simulations of Effect of Application Methods on Soil Methyl Bromide Emission

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ABSTRACT

Methyl bromide (bromomethane, MeBr), which originates from the oceans, fumigation, and a few other sources, is reportedly contributing to the ozone depletion in the stratosphere. Due to the heavy reliance on this fumigant in the production of many crops, it is of particular importance to accurately quantify the atmospheric input of MeBr arising from agricultural uses, and develop feasible measures to minimize these emissions. In this study, we determined the effect of two important application variables, surface tarp and injection depth, on MeBr transport and transformation in the soil and its emission from the soil surface under controlled conditions. Following 20- and 30-cm injections, covering the soil surface with 1-mil (0.025 mm) high-density polyethylene film resulted in an average of 48% reduction in MeBr emission. Increasing the injection depth from 20 to 60 cm caused a decrease in MeBr emission of 54% under untarped conditions and 40% under tarped conditions. The influence of application methods on MeBr atmospheric emissions should be considered when estimating the contribution of agricultural fumigation to the overall atmospheric MeBr burden on a global scale. The results also indicate that MeBr emission after soil fumigation may be substantially minimized by using surface tarpaulins and deep injections.

DURING THE PAST DECADE, there has been increasing concern about the effects on the stratospheric ozone layer of a variety of gases in the atmosphere. The Ozone Assessment Synthesis Panel of the United Nations Environmental Programme determined that the Antarctic ozone hole is primarily a result of the presence of Cl and Br containing chemicals in the atmosphere. Recently, much attention has been focused on methyl bromide (bromomethane, MeBr), because MeBr is the main source for atmospheric Br, while Br is believed to be much more efficient than Cl in breaking down ozone on a per atom basis (by a factor of ≈ 40; Wofsy et al., 1975). A recent assessment attributed 5 to 10% of the current global loss of stratospheric ozone to MeBr alone (Watson et al., 1992). There are a few known sources that contribute MeBr to the atmosphere, but none of them are well quantified and the reported values vary widely. It has been estimated that the production by marine plankton in the oceans contributes 50 to 80% and agricultural fumigation contributes 15 to 35 % (Abritton and Watson, 1992; Singh and Kanakidou, 1993; Khalil et al., 1993; Butler, 1995). However, recently it was debated that biomass burning may contribute up to 30% (Mano and Andreae, 1994), while the oceans may act as a net sink, rather than a source (Butler, 1994), and the deposition onto soil and subsequent microbial degradation may be another important pathway for removing MeBr from the atmosphere (Shorter et al., 1995). Since the emission from agricultural fumigation is the only controllable source, the use of MeBr in the USA is scheduled for phase out by the year 2001, and its use on the worldwide scale is also to be restricted (U.S. Environmental Protection Agency, 1993; Chakrabarti and Bell, 1993). However, the many uncertainties involved with the sources and sinks of atmospheric MeBr imply that more accurate estimates for the relative contribution from agricultural fumigation should be obtained to justify these decisions.

On the other hand, owing to its wide spectrum of activity against nematodes, fungi, bacteria, weeds, and insects, MeBr has been the fumigant of choice for the last few decades. The phase out of MeBr, if not replaced with equivalently effective fumigants or fumigation techniques, will cause serious economic damage to the agricultural communities (The National Agricultural Pesticide Impact Assessment Program, 1993; Ferguson and Padula, 1994). However, currently there is no single alternative that can perform to the standard of MeBr in soil-borne pest control (Ferguson and Padula, 1994; Noling and Becker, 1994). Under this circumstance, if application methods are developed that allow significantly less emission of MeBr without sacrificing efficacy, the proposed regulatory policies on MeBr may be postponed or exemptions may be made for certain situations. To design these low-emission methods, the controlling factors must be identified, and their relative contribution to the overall emission of MeBr must be quantitatively determined.

Two important variables related to the application of MeBr as a soil fumigant are the use of surface tarp and injection depth. The commonly used surface tarp is low or high density polyethylene film, and the injection depth varies from 25 to 70 cm, depending on the soil texture, crops, and distribution patterns of the target organisms. Most of the currently used application techniques, such as the use of polyethylene or other lesser permeable films, were originally developed with the objective of achieving adequate efficacy of control with lower dosages, or reducing the risk to workers (de Heer et al., 1983; Hamaker et al., 1983; Lembright, 1990). The relative influence of these factors on MeBr emissions has never been independently examined with experiments.

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Abbreviation: HDPE, high-density polyethylene film.

During the last few years, several field studies have been completed to obtain representative emission rates for MeBr, and the reported rates vary from 20 to 89% (Yagi et al., 1993, 1995; Majewski et al., 1995; Yates et al., 1996a,b; Yates et al., 1997). Apparently, very different experimental conditions are attributable to this great variability. Since numerous dynamic processes and factors influence the transport and volatilization of MeBr under field conditions, it is difficult, if possible at all, to determine the relative contribution from each individual factor. Studies under controlled conditions are thus needed to provide information for interpreting these variations. We have conducted a series of experiments to investigate interactions of MeBr volatilization with a number of important factors, including factors related to soil conditions (Gan et al., 1996) and factors related to application methods. In these experiments, volatilization rates of MeBr were measured from 60-cm soil columns under controlled conditions and then extrapolated to infinite depth scenarios using a vapor phase transport model. The influence of a specific factor on MeBr volatilization was investigated by varying this factor only while carefully keeping the other conditions unchanged. In a previous study, we observed that soil conditions, e.g., soil type, soil water content, and bulk density, had pronounced effects on MeBr transport and volatilization losses (Gan et al., 19%). In this study, we report the effect of two important application-related variables, i.e., surface covering with polyethylene film and injection depth. This information is useful for interpreting field observations, as well as for providing the rationale for developing optimized application methods that would produce minimum MeBr emissions but maintain adequate efficacy.

MATERIALS AND METHODS

Closed, Packed Soil-Column System

Figure 1 illustrates the column system used for studying MeBr vapor transport and volatilization after soil injection. It consisted of a packed soil column [62 cm high by 12.5 cm (i.d.), bottom-sealed] and a sampling chamber of the same diameter [3.5 cm high by 12.5 cm (i.d.), top-sealed], both made of glass. Sampling ports, which were made by installing thick Thermogreen septa (0.5 cm in diameter, Supelco Inc., Bellefonte, PA) in 0.4-cm openings, were positioned every 10 cm along the column, Soil used for packing the columns was taken from the 0- to 30-cm depths in the field on the University of California's Moreno Valley Field Station. The soil is a Greenfield sandy loam (coarse-loamy, mixed thermic Typic Haploxeralf) and has an organic matter content of 0.92 %, clay content of 9.5 %, pH (H_2O) of 7.4, external surface area of 14.4 $m^2 g^{-1}$ (N_2 adsorption method), and particle density of 2.67 $g cm^{-3}$. Air-dried soil was sieved through a 2-mm sieve, and the moisture content was adjusted to 9% by adding deionized water and equilibrating for more than 24 h in a closed container before use. The moist soil was packed carefully in 5-cm increments into the column to a predetermined bulk density. The soil surface in the packed column was ≈ 2 cm below the column opening. The sampling chamber was then carefully placed on the top of the soil column to form a closure, and the connection between the sampling chamber and the soil column was sealed with sealant-coated aluminum tape. To determine the effect of surface covering, a round piece of I-mil (0.025 mm) high density polyethylene film (HDPE, TriCal Co., Hollister, CA) with an area larger than the opening of the soil column was placed between the sampling chamber and soil column before the system was sealed. Cautions were exercised to make the connection between the plastic film and the wall of the column airtight. After the system was completely closed, an airflow of 150 mL min^{-1} was established through the inlet and outlet in the sampling chamber by connecting the outlet to a vacuum source. The airflow swept volatilized MeBr into the sampling tubes containing 600 mg coconut-based activated charcoal granules (ORBO-32 tubes, Supelco). At this flow rate, ideally, the air above the soil surface was exchanged once every 4 to 5 min. All the columns were kept in the laboratory at 23 ± 2°C during the entire experiment. Under the above conditions, it may be assumed that the dissipation of MeBr in the column was caused by volatilization that was measured above the soil surface and degradation during the experiment.

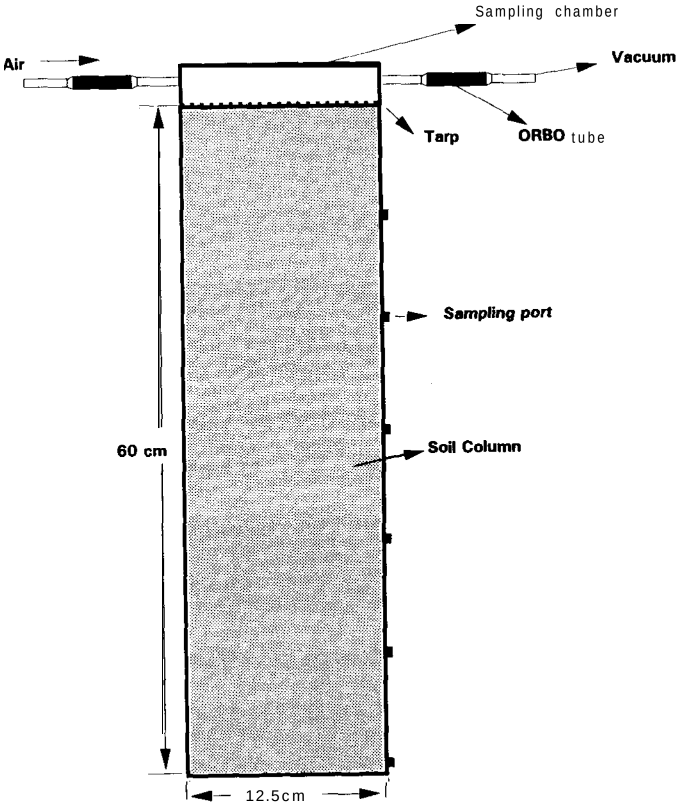

Fig. 1. Closed, packed-soil column system used for MeBr vapor transport and volatilization studies.

Three injection depths, 20, 30, and 60 cm, were included in this study. For applications at 20- and 30-cm depths, columns were prepared with untreated Greenfield sandy loam to provide the following conditions: bulk density (ρ_b) 1.40 ± 0.01 g cm^{-3}, total porosity (φ) 0.476 ± 0.015, volumetric water content (θ) 0.124 ± 0.003 $m^3 m^{-3}$, and volumetric air content (a) 0.352 ± 0.005 $m^3 m^{-3}$. For application at 60-cm depth, columns were prepared with untreated Greenfield sandy loam to give the following conditions: $\rho_b = 1.70 \pm 0.02$ g cm^{-3}, $\theta = 0.146 \pm 0.003$ $m^3 m^{-3}$, and a = 0.217 ± 0.003 $m^3 m^{-3}$. The higher bulk density and water content used for the deeper injections were to more closely represent the actual changes of bulk density and moisture content commonly seen along the soil profile in the field. In the field where the soil was sampled, the bulk density ranged from 1.30 to 1.60 g cm^{-3} for soil depths from 0 to 30 cm but increased to 1.65 to 1.70 g cm^{-3} for soil layers below 30 cm. The volumetric water content was 0.056 $m^3 m^{-3}$ from 0- to 10-cm depth, increased linearly to 0.145 $m^3 m^{-3}$ at 30-cm depth, and stabilized around 0.22 $m^3 m^{-3}$ for soil layers below 30 cm.

Methyl Bromide Application and Sampling

A series of experiments were conducted, and in each of them, two to four columns were run simultaneously by using a manifold with adjustable flow controllers (SKC West Inc., Fullerton, CA) to establish an identical air circulation for each column. To provide information on the reproducibility of using the packed column system in obtaining volatilization rates of MeBr, treatments were repeated for the untarped and tarped injections at 30 cm under the same conditions but in two separate experiments.

Before application, MeBr was introduced into a 500-mL Teflon sampling bag from a lecture bottle containing 99.5 % pure MeBr (Matheson Gas Products, Inc., East Rutherford, NJ). For shallow applications, 40 mL of the MeBr gas (3.9 mg mL^{-1} at 1.0 atmosphere and 25°C) was injected into the soil using a gastight syringe via a sampling port at 20 or 30 cm. For deep application, the same amount of MeBr was injected at 60 cm into the columns with a high bulk density (1.70 g cm^{-3}). The MeBr gas in the syringe was released within a few seconds into the soil ≈5 cm from the column wall. This rate of 156 mg column’ was equivalent to about a half of the typical field application rate of 200 to 300 kg ha-‘. The time that MeBr was injected into the soil was considered as time zero. After MeBr was applied, charcoal sampling tubes were changed every 0.5 h for the first 10 h and every 1 .O or 2.0 h thereafter except for the night hours between 11:30 p.m. and 7:30 a.m. when an 8.0-h interval was used. Changing sample tubes was generally completed within 1 min, during which the air circulation to the column was temporarily interrupted. The number of tubes in series was adjusted according to the length of sampling intervals, with more tubes being used for longer sampling intervals to eliminate breakthrough (Gan et al., 1995a). Sample tubes were stored at -4°C and analyzed for MeBr content within 48 h. Under these conditions, MeBr trapped on the charcoal was found to be stable and not affected by storage (Gan et al., 1995a).

At predetermined intervals, 0.5 mL of soil air was withdrawn at different depths via sampling ports using a 1 .O-mL side-port, push-button gastight syringe (Supelco). The air samples were directly transferred into 21-mL headspace vials, and the vials were crimp-sealed immediately with aluminum caps and Teflon-faced butyl-rubber septa (Supelco). Numerous tests in preliminary experiments showed that direct transferring of air samples containing MeBr into the deep part of open vials followed by immediate capping was quantitative and reproducible. Sampling of volatilized MeBr above the soil surface was continued until the concentration in the sample tubes was below detection limits. Upon termination, samples of soil were removed from different depths along the column and analyzed for Br- concentrations, soil water content, and bulk density. Since Br- is produced in both hydrolysis and methylation reactions of MeBr in soil, increases in Br- concentration at the end of the experiment over the background (0.15 mg kg-‘) can be used to calculate MeBr degradation ratios.

It must be noted that MeBr was applied differently in this study from the traditional injection method used in the field. During soil fumigation in the field, MeBr is applied in its liquid form in lines spaced 20 to 35 cm apart for shallow applications or 160 cm apart for deep applications. Immediately after the liquid MeBr enters the soil, it absorbs heat and becomes gaseous MeBr due to its very low boiling point (3.6°C) and extremely high vapor pressure (122 kPa or 1633 mm Hg). Therefore, the difference in applying MeBr could affect its distribution in soil at the very early stage.

Analysis of Methyl Bromide and Bromide

Charcoal tubes containing MeBr were analyzed using an optimized headspace-GC method on a Tekmar 7000 headspace autosampler (Tekmar Co., Cincinnati, OH) and a Hewlett Packard HP 5890 GC (Norwalk, CT) equipped with an electron capture detector (Gan et al., 1995b). In brief, the charcoal along with glass wool plugs and polyurethane spacers from the sampling tubes were transferred into 21-mL headspace vials. After 2 mL of benzyl alcohol was added, the vials were crimp-closed with aluminum caps and Teflon-faced butyl-rubber septa. The sample vials were then equilibrated in the headspace autosampler at 110°C for 15 min. At the end of equilibration, 1 .O mL of the pressurized headspace was automatically injected into the GC via a six-valve injection port and a heated transfer line. The GC conditions used in the study were Crossbond cyanopropylphenyl methyl polysiloxane phased RTX-624 column (25 m by 0.25 mm by 1.4 μm; Restek Co., Bellefonte, PA), 35°C oven temperature, 170°C inlet temperature, 240°C detector temperature, 1 .O mL min^{-1} carrier flow (helium), and 1:20 split ratio. Calibration curves were made by analyzing charcoal tubes spiked with known amounts of MeBr gas (0.2-2000 μL) under the same conditions. Closed headspace vials containing soil air samples were also analyzed on the headspace autosampler-GC under the same conditions except no solvent was added in the vials. Calibration curves were made by analyzing vials containing known amounts of MeBr gas (0.01-6.0 μL) under the same conditions.

To determine Br- concentrations at the end of experiment, two 50.0-g soil samples were extracted with 50-mL of deionized water in 125-mL glass jars by mixing and settling the samples overnight. The supematant collected after centrifugation was analyzed for Br- concentration on a QuikChem AE automated ion analyzer (LaChat, Milwaukee, WI).

Extrapolation of Measured Emission Rates to Field Conditions

Since the column system used in this study was sealed at the bottom, downward penetration of MeBr was restricted to 60 cm. In a field study, trace MeBr gas was detected several meters below the surface following an untarped 68-cm injection (Yates et al., 1997). Unless extremely long columns are used, the overestimation of emission rates caused by the restricted lower boundary condition should be corrected. In this study, the measured volatilization rates were extrapolated to field-like, infinite lower boundary scenario using a gas-phase transport model. In brief, under both column and infinite lower boundary conditions, MeBr gas-phase diffusion can be described by the following model (Jin and Jury, 1995; Jury et al., 1983; Yates et al., 1997):

$$\frac{\partial C_g}{\mathrm{at}} = D_e \frac{\partial^2 C_g}{\partial x^2} - \mu C_g \qquad [1]$$

$$C_g(x,0) = C_0[u(x - x_1) - u(x - x_2)] \qquad [2]$$

$$\left.\frac{\partial C_g}{\partial x}\right|_{\mathrm{lower}} = 0 \qquad [3]$$

$$-D_e \frac{\partial C_g}{\partial x}\bigg|_{\text{upper}} = -h[C_g - C_{\text{chamber}}] \qquad [4]$$

Where Eq. [2] through [4] define the initial, lower, and upper boundary conditions, respectively; C_g is the vapor concentration, D_e is the effective diffusion coefficient, μ is the degradation rate constant, x is the distance, t is the time, $\mu(x)$ is a Heavyside unit step function, h is a mass transfer coefficient across the surface boundary layer, C_0 is the initial concentration after injection, and C_{chamber} is the concentration inside the sampling chamber. It is assumed in Eq. [2] that the liquid phase during the experiment is immobile, a reasonable assumption given the low moisture content of the soil and the time scale of the experiment.

To extrapolate the column measurements to infinite lower boundary conditions, three steps were used. First, D_e and C_0 were estimated by simultaneously fitting multiple sets of the measured soil gas phase MeBr concentrations at different depths to the above transport model for column conditions, using the nonlinear least-squares minimization technique. In the second step, the estimated D_e and C_0 were incorporated in the above model to generate estimates of total MeBr volatilization losses for both column and infinite lower boundary situations. Finally, the ratio of these two estimates was calculated and used as a correction factor to extrapolate column measurements to infinite depth.

One advantage of this experimentation-simulation approach compared with a simple laboratory study is that after extrapolation, the laboratory measured data have implications for field situations and the results may be compared with the measured field emission rates, which in turn, validates the estimates. The main advantage of this approach compared with the traditional model simulation is that the model parameters are generated directly from the experiment, rather than estimated from literature or determined independently. This should increase the accuracy of the modeling results.

RESULTS AND DISCUSSION

Effect of Surface Tarp on Methyl Bromide Emission

Since soil columns used in this study had similar characteristics (e.g., same soil type and soil water content), differences in MeBr behavior could be attributed only to the variation intentionally introduced in application methods, e.g., change in surface conditions (tarped vs. untarped) or injection depth. Figure 2 shows MeBr volatilization fluxes in milligrams (MeBr) per hour per column, and Fig. 3 gives the cumulative MeBr volatilization losses in percentage of applied MeBr for both tarped and untarped treatments following injections at various depths. In Fig. 2b and Fig. 3b, MeBr volatilization fluxes and cumulative losses from two replicate treatments after 30-cm injections are compared. In these and some other replicated experiments (data not shown), it has been consistently found that when the parameters of the packed column (e.g., soil type, bulk density, and soil water and air contents) were carefully controlled, measured volatilization rates of MeBr were highly reproducible. This may be partly due to the elimination of water movement in the column during the experiments and the lack of significant effect of the column wall or preferential flow on solute transport as often encountered in leaching studies using packed soil columns. Therefore, differences in MeBr volatilization behavior observed among the different treatments in this study may be mainly attributed to the varied surface condition or injection depth.

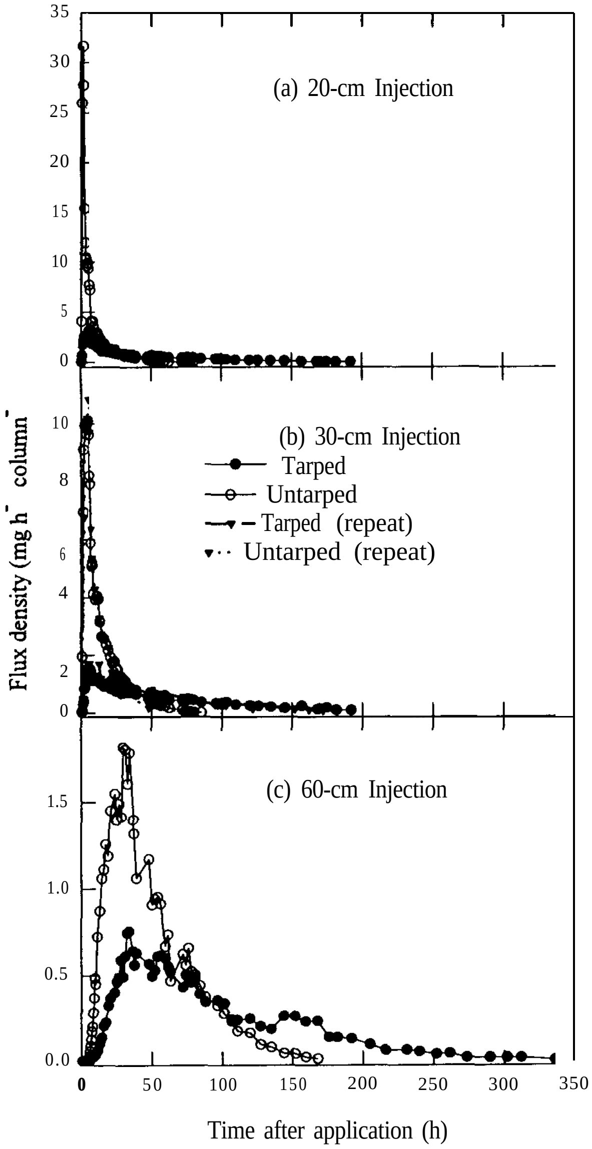

Fig. 2. Methyl bromide volatilization fluxes following application under polyethylene film-tarped and untarped conditions: (a) 20-cm injections; (b) 30-cm injections; (c) 60-cm injections.

Following the 20-cm injections, the total volatilization loss of MeBr was 91% under bare surface conditions and 59% under tarped surface conditions (Fig. 3a). For the 30-cm injections, 83% of the applied MeBr was emitted for the untarped column, while ≈ 52% was lost for the tarped column (Fig. 3b). When the soil surface was not tarped with the polyethylene film, MeBr volatilization was extremely rapid immediately following the application, with most of the volatilization loss (80-91%) occurring during the first 24 h (Fig. 2a and 2b). In contrast, when a tarp was present on the soil surface, the maximum volatilization flux was significantly smaller, with only 3 1 to 44 % of the overall volatilization happening within the first 24 h (Fig. 2a and 2b). Methyl

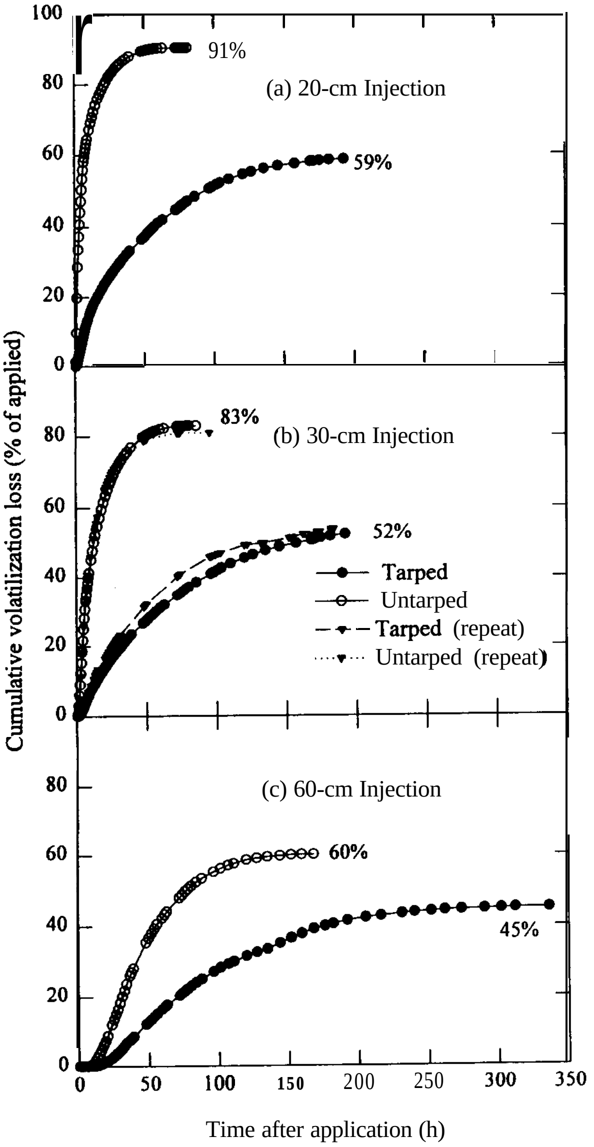

Fig. 3. Cumulative MeBr volatilization losses following application under polyethylene film-tarped and untarped conditions: (a) 20-cm injections; (b) 30-cm injections; (c) 60-cm injections.

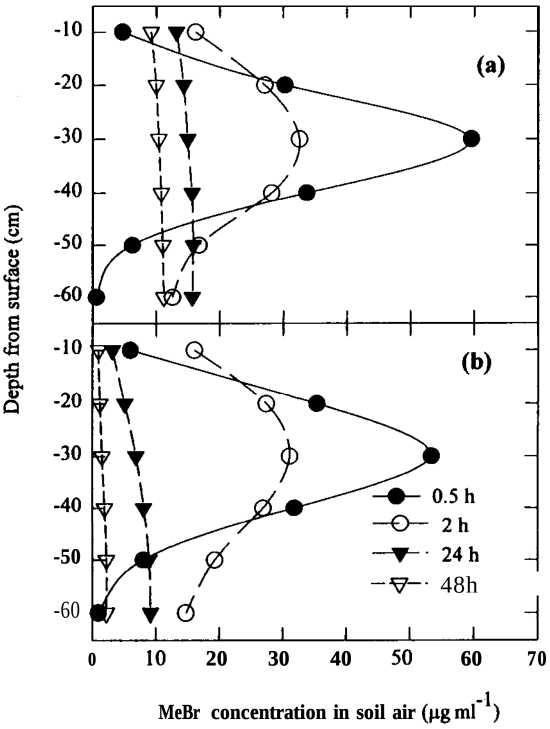

Fig. 4. **Methyl bromide distribution in the soil gas phase following 30-cm injections: (a) untarped application; (b) tarped application.**

bromide volatilization from tarped columns decreased more gradually and measurable volatilization continued for a considerably longer time (7-10 d) than from the untarped columns (3-4 d). Under field conditions, much higher fluxes of MeBr were measured during the initial hours across an untarped field than across a tarped field, and measurable volatilization stopped ≈ 5 d after the fumigation for the untarped field, but continued for 9 d for the tarped field (Majewski et al., 1995). Following the 60-cm injection in the same soil, the total volatilization loss was 60% under bare surface conditions, and 45 % under tarped conditions (Fig. 3c). Volatilization of MeBr lasted for 7 d in the untarped column but continued for 14 d in the tarped column (Fig. 2c).

Periodic measurement of MeBr concentrations in the soil gas phase at different depths along the soil column revealed the spatial distribution and dissipation trends of MeBr after application. Soil gas phase concentrations along the column following 30-cm applications are used as examples in Fig. 4 to illustrate the effect of surface tarp on MeBr volatilization behavior. After MeBr was injected into the soil at 30 cm, it diffused rapidly upward to the soil surface and downward to the bottom of the column through the soil gas phase (Fig. 4). Although the initial MeBr spatial distribution patterns were similar in both of the tarped and untarped columns, in the untarped column (Fig. 4b), MeBr near the surface was rapidly lost through the unrestricted surface and its concentration in the soil gas phase decreased below the detection limit shortly after application. But when the soil surface was covered with the polyethylene sheet, MeBr was apparently held in the soil for a significantly longer time (Fig. 4a). For instance, the concentration at 10 cm from the surface was consistently greater in the tarped column than that in the untarped column a few hours after the application, indicating that MeBr accumulated below the tarp. When applied at 51 cm, Abdalla et al. (1974) also found that the presence of a polyethylene cover resulted in a fourfold increase in MeBr concentration at 30-cm depth compared with an untarped treatment. These observations indicate that though polyethylene is known to be somewhat permeable to MeBr, it clearly acted as a temporary barrier to prevent MeBr from quickly escaping out of the soil surface.

With the use of Henry's law constant K_H for MeBr (0.25 at 25°C), the experimentally determined MeBr adsorption coefficient K_d between soil and water phases (0.1 $cm^3 g^{-1}$), and the measured MeBr concentration in the soil gas phase, the total MeBr mass remaining in the soil-water-air phases in the column was calculated with the following equation:

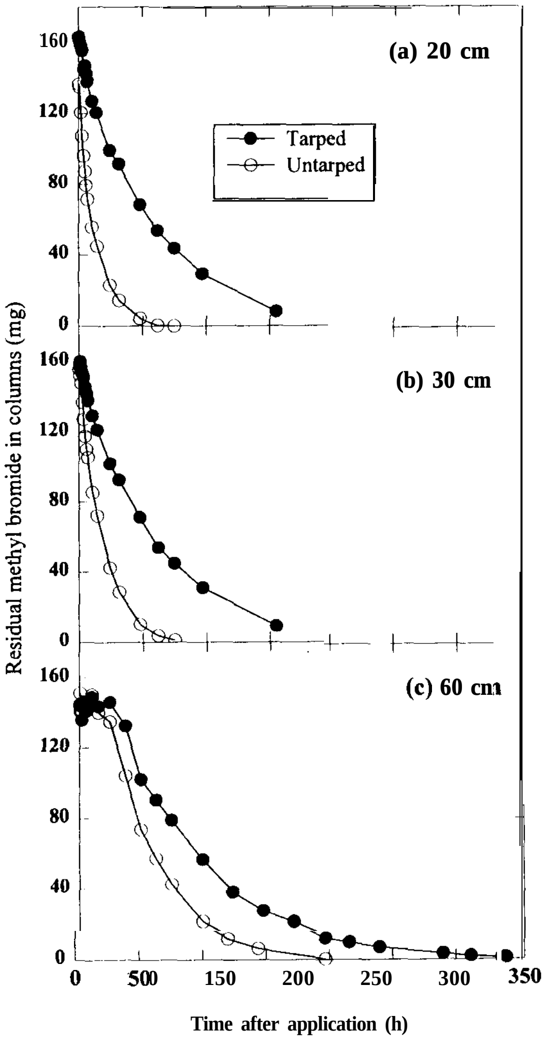

Fig. 5. Dissipation of total MeBr from soil columns following application under polyethylene film-tarped and untarped conditions: (a) 20-cm injections; (b) 30-cm injections; (c) 60-cm injections.

$$M = C_a aV + \frac{C_a}{K_H}\theta V + \frac{K_d C_a}{K_H}\left(\frac{\varrho_b}{\varrho_p}V\right) \qquad [5]$$

Where M is the total MeBr mass remaining in the soil; C_a is the measured MeBr concentration in soil air; V is the total volume of the soil column (7360 cm^3); ϱ_p is soil particle density in g cm^{-3} (2.67); and a, ρ_b, K_H, and K_d are as defined above. At equilibrium, in soil with 1.40 g cm^{-3} bulk density and 0.124 $m^3\,m^{-3}$ volumetric water content, it was estimated that 33% of the total MeBr in the soil column was in the gas phase, 47% was dissolved in the soil water, and 20% was adsorbed on the soil solid phase. In columns with 1.70 g cm^{-3} bulk density and 0.146 $m^3\,m^{-3}$ volumetric water content, distribution of MeBr in the gas, water, and solid phases was 21, 55, and 24%) respectively. The dissipation of total MeBr in the columns after application is shown in Fig. 5. It can be observed that MeBr was consistently retained longer in the tarped columns than in the untarped columns following injections at the same depths. For instance, at 24 h after application, only 17 and 31% of the applied MeBr remained in the untarped columns for the 20- and 30-cm injections, respectively, but 64 and 66% still remained in the tarped columns treated at the same depths. Similar effects were also observed for the 60-cm applications. For instance, at 48 h, ≈47% of the applied MeBr remained in the untarped column, while 65% remained in the tarped column.

Table 1. Methyl bromide emission rates and mass recoveries from soil columns under various application conditions (in percentage of applied).

Injection depth	Emitted (measured)	Degraded	Mass balance	Emitted? (extrapolated)
cm				
		Tarped columns		
20	59	36	94	43
30	52	39	91	37
60	45	46	91	26
		Untarped columns		
20	91	12	102	82
30	83	15	98	71
60	60	36	96	38

† Emission rates after extrapolated to infinite depth.

From the above evidences, tarp consistently increased the time and amount of MeBr residing in the soil. The prolonged retention of MeBr in the soil should result in more extensive degradation. This is confirmed by amounts of MeBr degraded in the soil as measured at the end of the experiment by analyzing for Br- (Table 1). More degradation consistently occurred in the tarped columns than in the untarped columns for all the injection depths. This further indicates that although the polyethylene film used for the surface cover is permeable to MeBr, it poses a significant short-term barrier; MeBr volatilization was reduced in the tarped columns because more extensive degradation occurred due to the prolonged retention of MeBr in the soil.

After correcting for the lower boundary conditions and extrapolating the measured emission rates to infinite lower boundary situations, surface tarp caused ≈ 47% reduction in MeBr volatilization for the shallow applications and 33 % for the 60-cm applications (Table 1). The difference between extrapolated and measured emission losses is greater for the tarped column than for the untarped column when the application depth is the same. For instance, the extrapolated loss is 72 % of the measured value for the tarped, 20-cm injection but 90% for the untarped, 20-cm injection (Table 1). The presence of polyethylene film on soil surface clearly encouraged the downward movement of MeBr in soil profile. In field measurements (Abdalla et al., 1974) and model simulations (Rolston and Glauz, 1982), it was observed that MeBr moved deeper in soil profiles when the surface was tarped. Similar effect of surface cover on MeBr volatilization losses was found in two parallel field experiments (Majewski et al., 1995). In an untarped field, MeBr emission after 25- to 30-cm injection was measured to be 89% during the first 5 d after application, while in a tarped field located 6 km away, the emission rate was 32% during the first 9 d after application. Based on the results from this study and the few reported field studies, it can be concluded that for shallow applications (20-30 cm), MeBr emission rate in a tarped field is considerably smaller than that in an untarped field when the other conditions are the same. Since currently most soil fumigation practices are carried out under tarped conditions (United Nations Enviroment Programme, 1995, p. 37-38), a smaller rate than the commonly assumed 80 to 85% should be adopted when estimating the relative contribution of atmospheric MeBr from agricultural fumigations. Nevertheless, it has to be realized that polyethylene plastics may still be too permeable to MeBr. In a laboratory study where a 20-cm soil column was used, polyethylene film showed negligible effect in preventing MeBr volatilization losses (Jin and Jury, 1995). The use of a short column in which degradation was limited might have partly contributed to this observation. The relative ineffectiveness of the commonly used polyethylene plastic in reducing MeBr volatilization was also demonstrated in model simulations (Rolston and Glauz, 1982). To further reduce MeBr emission, films with lower permeability should be used. Lesser permeable films such as Saranex replaced low density polyethylene film in glasshouse fumigation after 198 1 in the Netherlands, and lower MeBr emissions have been reported (de Heer et al., 1983; Hamaker et al., 1983; Wegman et al., 1983). Since MeBr is retained in the soil much longer under these relatively impermeable films, it was also possible to reduce the application rate from 50 g m^{-2} to 20 g m^{-2} without sacrificing the efficacy (Hamaker et al., 1983). Jin and Jury (1995) suggested the use of surface cover in combination with irrigation to reduce MeBr volatilization. After three consecutive simulated irrigations in a soil column, only 4 % of the treated MeBr was emitted through soil surface. The plastic cover kept water from vaporizing from the soil surface, and the formed saturated surface soil layer worked effectively to reduce gaseous diffusion of MeBr through the surface.

Effect of Injection Depth on Methyl Bromide Emission

The effect of application methods in this study can also be analyzed from the perspective of injection depth. From Fig. 3, when injection depth was increased from 20 to 30 cm and then to 60 cm, the measured MeBr emission rate decreased from 91 to 83 % and further to 60 % under untarped conditions and from 59 to 52 % and further to 45 % under tarped conditions. In the untarped columns (Fig. 2), the maximum volatilization flux became smaller following deeper injections, decreasing from 31 mg h^{-1} column-' for the 20-cm injection to only 1.8 mg h^{-1} column-^{1} for the 60-cm injection. Volatilization flux also reached the maximum at a later time for deeper injections, as reflected in the delay from 1.5 h for the 20-cm injection to 29 h for the 60-cm injection. Similar but lesser effects of injection depth on MeBr volatilization flux were also observed for the tarped treatments (Fig. 2). It must be pointed out that to simulate field conditions, the columns used for the 60-cm applications were packed at a higher bulk density and water content. Therefore, the observed effect of deep injection on MeBr volatilization was truly a result of the collective effects of the increased injection depth, soil bulk density, and soil water content. Increasing soil bulk density and water content decreased volumetric air content and therefore might have restricted MeBr diffusion in the soil gas phase. Measured Br- accumulation at the end of the experiment indicates that more degradation occurred in the soil when MeBr was applied at a greater depth, under both untarped and tarped conditions (Table 1).

After extrapolating the measured emission rates to infinite depth, when the application depth was increased from 20 to 60 cm, MeBr emission rates decreased by 54 % under untarped conditions and 41% under tarped conditions (Table 1). The corrected MeBr emission rate for the tarped, 60-cm application of only 26% was the lowest loss observed from any of the treatments (Table 1). The difference between the extrapolated and measured emission losses increases with increased application depth under either tarped or untarped conditions. For instance, under untarped conditions, the extrapolated loss is 90% of the measured value for the 20-cm injection but decreased to only 63% for the 60-cm injection. This suggests that under infinite depth conditions (as in the field), deep placement of MeBr will result in more MeBr distribution in the deeper layers. Abdalla et al. (1974) found that application at 76 to 81 cm without soil cover resulted in gas distribution at concentration sufficient for nematode kill as deep as 244 cm. By placing MeBr at 90 cm, Kolbezen et al. (1974) detected adequate dosages at 300 to 360 cm. Though these early studies were only designed for obtaining information on nematode control in deep soil layers, they indicate that by deep application, MeBr downward diffusion is encouraged or upward diffusion is reduced. The results from this study are also in agreement with predictions made by using model simulations (Reible, 1994), and the emission rate obtained in a recent field experiment where MeBr was applied at 68 cm under untarped conditions (Yates et al., 1997). Under assumed conditions, Reible (1994) estimated that by increasing injection depth from 25 to 45 cm, MeBr emission rates should decrease from 45 to 28 % under tarped conditions. In the field experiment, only $\approx$ 20 % of the applied MeBr was emitted in a field that has the same Greenfield sandy loam as used in the current study (Yates et al., 1997). From these findings, it can be concluded that placing MeBr at a greater depth is another effective approach for minimizing its emission into the air during soil fumigation.

Deep placement of MeBr in coarse-textured soils is usually efficacious (Lembright, 1990; Abdalla et al., 1974). Application to the heavy-textured subsoil may be less effective, particularly if the soil is saturated at that depth. Therefore, to what depth MeBr may be actually injected is dependent on soil conditions and the distribution pattern of target organisms, and should be decided by weighing between the efficacy and emissions under certain circumstances.

CONCLUSIONS

We demonstrated in a previous study that variations in soil conditions (e.g., soil type, soil water content, and bulk density) influenced MeBr emissions from soil. In this study, the effects of application methods on MeBr emissions have been assessed. These effects may have two important implications. First, the dependence of MeBr emission rates on application methods should be taken into consideration when estimating the contribution from agricultural use of MeBr to the overall MeBr load in the atmosphere. The commonly assumed 80 to 85% emission loss following soil fumigation with MeBr may be an overestimation for tarped applications. Since more than 85 % of the fumigations in the USA, and nearly all of the fumigations in the other countries, are conducted under tarped conditions (United Nations Environment Programme, 1995, p. 37-38), adoption of a lower emission rate may be more appropriate. To obtain more accurate estimates of the contribution from the agricultural use of MeBr, statistical data on the acreage of fumigation and the variations of application methods should be gathered and different emission rates should be applied. Second, these factors may be exploited for minimizing MeBr emissions from fumigated fields. By combining deep placement and use of a surface tarp, MeBr emissions can be substantially reduced from the current level. This and a few other studies indicate, however, that the commonly used polyethylene film may still be too permeable for MeBr to arrive at a negligible emission rate. To further reduce MeBr emissions, it is imperative to investigate the possibility of substituting polyethylene sheets with tarp materials of lower permeability to MeBr or combining surface covering with other management practices such as surface irrigation (Jin and Jury, 1995). The impact of surface tarp and deep placement on the efficacy of MeBr should be considered along with their usefulness in emission reduction.

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