

Temperature Effect on Methyl Bromide Volatilization: Permeability of Plastic Cover Films

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ABSTRACT

Conventional methods of applying methyl bromide (MeBr) for soil fumigation can result in significant losses to the atmosphere, potentially contributing to the depletion of stratospheric ozone. It has been found that one of the major factors controlling MeBr volatilization is the permeability of the plastic cover films. Since the most commonly used agricultural film (i.e., polyethylene or PE) is not effective in containing MeBr, one practical method of reducing MeBr volatilization is to replace the PE film with one that is less permeable to MeBr. In this study, we document the temperature-dependent permeability of standard PE and a new plastic film (Hytibar) that is considered to be virtually impermeable to MeBr. Functional relationships between temperature and the film permeability to MeBr were obtained from a calibration experiment under controlled conditions. A field experiment was conducted to determine MeBr volatilization dynamics from plots covered with the two different plastic films. A diffusion-based transport model was used to simulate the fate and transport of MeBr gas in the soil and volatilization into the atmosphere. In both the calibration and field experiment, the Hytibar film was found to be nearly impermeable to MeBr. Volatilization of MeBr was affected directly by temperature changes of the PE or Hytibar film in the calibration experiment. Under field conditions, MeBr emission was less affected by temperature, especially at large times after application. Model simulation predicted MeBr volatilization reasonably well for the PE covered field plot, but overpredicted the emission for the Hytibar plot.

CURRENT fumigation practices can cause 21 to 87% of the applied MeBr to be lost to the atmosphere after soil fumigation (Yagi et al., 1993, 1995; Yates et al., 1996a, b, c, 1997; Majewski et al., 1995). There is a need either for alternative management methods that are effective in reducing MeBr volatilization, or for alternative chemicals that could replace MeBr while maintaining effective pest control and without environmental adverse effects. The search for alternative fumigants requires detailed laboratory and field testing and a lengthy registration process.

The amount and rate of MeBr volatilization from soil fumigation have been found to be strongly affected by soil, atmospheric, and managerial variables. Since MeBr moves in the soil predominantly in the gaseous phase, reducing soil porosity by increasing soil moisture content or bulk density would retard MeBr movement to the soil surface (Gan et al., 1996) where emission into the atmosphere occurs. Increasing MeBr application depth in the soil can increase the travel distance to the soil surface along with the resident time for degradation, therefore reducing total emission (Yates et al., 1997; Gan et al., 1997; Reible, 1994). Atmospheric variables

that are important to MeBr volatilization may include solar radiation, air and soil temperature, barometric pressure, wind speed, and relative humidity. Wang et al. (1997c) showed through modeling that the dynamic processes of MeBr volatilization are strongly influenced by soil or air temperature variations. By incorporating temperature dependence of transport parameters and PE film permeability, they showed that the diurnal cyclic behavior in MeBr emission flux density could be predicted with a diffusion-based numerical transport model.

To meet the urgent need of reducing MeBr input into the atmosphere, a simple and practical alternative is to use a film that is much less permeable to MeBr than the conventional PE films. An important advantage of this approach is that it requires the fewest changes in current fumigation application practices. In fact, it has been long known (Kolbezen and Abu-El-Haj, 1977; Houck and Mackey, 1989; Yates et al., 1996d), that materials such as Mylar, Saran, or aluminum foil are much less permeable to MeBr than the PE films. In addition, newer plastics such as the Hytibar (Klerk's Plastic, Hoogstraten, Belgium) have been developed that incorporate a barrier polymer: ethylene vinyl alcohol (EVOH) between two layers of PE and have been shown to have a very low permeability to MeBr under laboratory conditions (Daponte, 1995; Yates et al., 1996d). The Hytibar film also appears to have physical and mechanical properties that are similar to the PE films, making it feasible for field use. Using an EVOH-film, effective control of fungal pathogens was achieved with only 40% of the regular dosage in Israel (500 kg/ha), whereas only 20% mortality was obtained with the PE film at the reduced rate (Gamliel et al., 1993, 1997). This would indicate that a high barrier film can reduce MeBr emission loss, hence increasing MeBr pest control efficacy. A field experiment with indirect emission estimates also indicated the potential effectiveness of the Hytibar plastic for reducing MeBr emissions (Wang et al., 1997a).

The permeability of PE films to MeBr has been found to increase very significantly with increasing ambient air temperature (Kolbezen and Abu-El-Haj, 1977; Yates et al., 1996c). This is a primary cause for large MeBr emission fluxes near solar noon when the temperature is high and for the lower emission rate observed at night when the temperature is low (Majewski et al., 1995; Yates et al., 1996a). Therefore, most emission loss is attributed to times when the temperature is high or permeability of the PE films is large.

The potential effectiveness of a highly impermeable barrier such as the Hytibar film in reducing MeBr vola-

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Abbreviations: MeBr, methyl bromide; PE, polyethylene; EVOH, ethylene vinyl alcohol; GC, gas chromatograph; HSA, headspace autosampler.

tilization would make its use an effective measure in controlling MeBr emission into the atmosphere. It is important to determine whether its permeability to MeBr is also temperature dependent and how it would be affected by diurnal temperature changes, as compared to the PE films. To answer these questions, we first obtained functional relationships between temperature and permeability of a PE and the Hytibar films to MeBr with a calibration experiment under controlled conditions. Then, a field plot experiment was conducted to compare the volatilization dynamics of MeBr when covered with the PE and Hytibar films. Finally, a computer simulation, using the temperature-film permeability relationships from the calibration, was used to predict the fate and transport of MeBr for the field experiment.

MATERIALS AND METHODS

Temperature-Dependent Film Permeability

To determine temperature effect on film permeability, a calibration experiment was conducted using a completely closed system similar to that reported by Wang et al. (1997b). The system (shown in Fig. 1) included a flow-through flux chamber, an enclosure that served as a MeBr source, and an air flow system for sampling the chamber and MeBr emissions. The flux chamber was placed onto the source enclosure after a layer of PE or Hytibar (both ~0.035 mm thick) was sealed over the opening of the enclosure.

The MeBr emission from the source to the overlaying flux chamber can be described as

$$J_M = h(C_e - C_a) = \frac{D_a}{d}(C_e - C_a) \quad [1]$$

where J_M is MeBr volatilization flux density [$M/(L^2 - T)$]; h is a mass transfer coefficient (L/T) which can be represented by the ratio of MeBr diffusion coefficient in air D_a (L^2/T) over an effective boundary layer thickness, d (L); C_e is MeBr concentration inside the enclosure (M/L^3); and C_a is MeBr concentration in the air stream flowing through the chamber (M/L^3). According to Wang et al. (1997c), the mass transfer coefficient or effective boundary layer thickness is attributed primarily to resistance from the plastic film and its dependency on temperature which can be described with a form similar to the Arrhenius equation. Since both D_a and d are temperature dependent, Eq. [1] can be rewritten as

$$J_M = \frac{D_a(T_a)}{d(T_a)}(C_e - C_a) \\ = \frac{4.9943 \times 10^{-10} T_a^{1.75}}{d^{Tr}} \exp\left(\frac{T_r - T_a}{RT_a T_r} E_a^d\right) (C_e - C_a) \quad [2]$$

where J_M is in $\mu\text{g}/(\text{m}^2 \text{ s})$; T_a is the air or film temperature ($^\circ\text{K}$); d^{Tr} is the effective boundary layer thickness at a reference

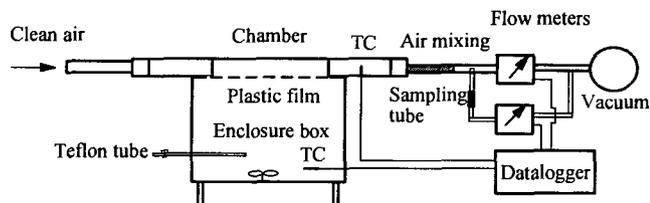


Fig. 1. Schematic of an air flow and sampling system for determining temperature effect on plastic permeability of methyl bromide volatilization.

temperature (T_r); E_a^d is the activation energy for the effective boundary layer thickness (J/mol); and R is the universal gas constant [$= 8.314 \text{ J}/(\text{mol}\cdot\text{K})$].

Therefore, the task is to determine d^{Tr} and E_a^d for PE and the Hytibar film, respectively. While J_M is directly calculated from the flux chamber measurement, C_a is also estimated from the flux samples averaged over each sampling interval (3 h). To measure MeBr gas concentration in the source enclosure (i.e., C_e), a small Teflon tube was inserted through a port on the source enclosure and sealed off from leakage (Fig. 1). The tube was also used to inject MeBr into the enclosure. A small electric fan was installed in the source enclosure to mix MeBr gas and obtain an even distribution in MeBr concentration inside the enclosure. Activated carbon tubes were used to adsorb MeBr for the emission measurement and MeBr concentration sampling from the source enclosure. A Hewlett-Packard 5890 gas chromatograph (GC) with electron capture detector was used for the analysis of MeBr content absorbed on each sampling tube. Injections were made from a Tekmar 7000 headspace autosampler (HSA) equipped with a 7050 sample carousel. More detailed descriptions of sample analysis can be found in Gan et al. (1994). Thermocouples were installed in the chamber and inside the enclosure to measure air temperatures (T_a) which was used as an estimate for temperatures of the two plastic films.

Field Determination of Methyl Bromide Volatilization

The field experiment was conducted in two experimental plots located on a University of California Agricultural Experimental Station near the Riverside campus. The soil is an Arlington fine sandy loam (a coarse-loamy, mixed, thermic Haplic Durixeralf). The particle-size distribution consists of 63% sand, 30% silt, and 7% clay. Each plot was about 3.4 by 4.9 m with four layers of continuous plastic films (two layers of Hytibar sandwiched between two PE films) buried vertically to 3 m depth along the perimeter of each plot. This kept MeBr gas from moving laterally away from the treatment zone and simulated large-scale field conditions. A detailed description of plot construction can be found in Wang et al. (1997a). Prior to MeBr application, one plot was covered with the PE film and the other with the Hytibar film, which was sealed to the side wall plastic. For each plot, MeBr gas was injected on 1 Oct. 1996 between 1030 to 1100 h at 25 cm depth through 10 buried drip irrigation tapes installed at a 0.31 m spacing. Method of injection followed the "hot-gas" injection procedures: liquid MeBr was converted to gaseous MeBr through a heat exchanger. Application rates were 28 and 21 g/m^2 for the PE and Hytibar plot, respectively. Less MeBr was applied for the Hytibar covered plot than for the PE plot. The intention was to efficiently use or conserve MeBr since Hytibar was much less permeable, hence less losses to the emission. The amount of MeBr emission has been reported to be proportional to the amount of MeBr applied (Yagi et al., 1995; Yates et al., 1996a; Majewski et al., 1995). Therefore, the different rate of application should not affect the emission assessment through the two plastic films. Precise dosage was achieved by weighing predetermined amounts of MeBr into separate containers, one for each plot, and injecting all MeBr from one container into the assigned plot. Nitrogen was used to purge the injection systems after MeBr application for each plot. A pressure of about 12 psi was maintained on the drip tapes during MeBr injection and purging with N. The overall injection process took about 1 min for each plot. This implies that the injected volume (MeBr + N gas) was about 0.2 m^3 .

Immediately after injection, MeBr emission was continu-

ously measured with two flow-through flux chambers placed about 1.5 m apart on each plot. An air flow and sampling system similar to the calibration setup was used. Ambient air of 10 m away from the plots was drawn, via a 5-cm diam. aluminum pipe, through the chambers with a vacuum and produced an average horizontal velocity of 1.3 cm/s across the sampling section of the chambers. Methyl bromide was subsampled continuously from the effluent air stream passing through the chambers. An air flow of approximately 120 mL/min was drawn through activated carbon tubes that absorbed MeBr present in the effluent air stream. We chose this flow rate because it would provide an amount of MeBr that can be accurately collected and analyzed for the current application rate. The sampling tubes were replaced every 3 h to obtain an assessment of the dynamic processes of the emission flux density. After collection, the samples were brought back to the laboratory in a portable ice-packed cooler and analyzed for MeBr content. Air and soil temperatures were measured by installing thermocouples inside the chambers and in the soil at different depths.

Soil-air profile samplers were installed for measuring MeBr gas concentration distribution. A 2-m sampler was installed in the center of each plot with sampling ports located at 0, 0.05, 0.15, 0.25, 0.35, 0.5, 0.75, 1, 1.5, and 2 m depths. Samples were taken at selected times after MeBr application by drawing 20 to 60 mL soil air through the charcoal tubes. Methyl bromide in the emission and soil air samples was analyzed with the same GC-headspace setup as used for the calibration system.

Simulation of Methyl Bromide Transport and Volatilization

Two distinctively different transport mechanisms controlled MeBr movement during and after application. Since MeBr was applied with the "hot-gas" method under a pressurized system, MeBr was transported primarily through convection during the injection process that lasted about 5 min (~1 min for MeBr injection and 4 min for system purging with N). Diffusion would be the major mechanism causing MeBr to move away from the sources after the pressurized injection.

The one-dimensional convective gas or vapor transfer in a porous media can be described as:

$$J_a = -K_a \frac{dP}{dx} \quad [3]$$

where J_a is the convective gas or vapor flux (L/T); K_a is the air permeability of the porous media (L/T); and dP/dx is the pressure gradient. One way to estimate K_a is to use soil hydraulic properties and the apparent volumetric soil water content (θ) as in Corey (1986)

$$K_a = K_s (1 - S_e)^2 (1 - S_e^\gamma) \quad [4]$$

where K_s is soil hydraulic conductivity under saturation (L/T); S_e is the apparent degree of water saturation, which is defined as $(\theta - \theta_r)/(\theta_s - \theta_r)$ where θ_r and θ_s are, respectively, the residual and saturated water content; and γ is a parameter indicative of soil structure.

After the initial convective flow during the pressurized injection, MeBr would move primarily by diffusion that can be described with (Simunek and van Genuchten, 1994)

$$\frac{\partial \theta C_L}{\partial t} + \frac{\partial \rho C_s}{\partial t} + \frac{\partial a_s C_g}{\partial t} = \theta D_L \frac{\partial^2 C_L}{\partial x^2} + a_s D_g \frac{\partial^2 C_g}{\partial x^2} - \frac{\partial q C_L}{\partial x} - \mu_L \theta C_L - \mu_s \rho C_s \quad [5]$$

where C_L , C_s , and C_g are MeBr concentrations in the soil in liquid (M/L^3), solid (M/M), and gaseous (M/L^3) phases, respectively; ρ is soil bulk density (M/L^3); a_s is soil air content (L^3/L^3); D_L and D_g are, respectively, MeBr effective diffusion coefficient in soil water and air phases (L^2/T); q is volumetric liquid flux density (L/T); μ_L and μ_s are first-order degradation rate constants for MeBr in liquid and solid phases ($1/T$); t is time (T); and x is distance (L). Instantaneous equilibrium is assumed for MeBr in liquid, solid, and gaseous phases. The liquid flux density q is calculated with the Richards' equation (Jury et al., 1991)

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left[K(h) \frac{\partial h}{\partial x} \right] - \frac{\partial K(h)}{\partial x} \quad [6]$$

where $K(h)$ is soil hydraulic conductivity (L/T) under a water potential h (L).

Heat transfer in the soil is accounted as conduction and convection coupled with liquid flux, neglecting the relatively insignificant diffusive heat movement through water vapor. Therefore, a one-dimensional heat transport equation can be described as (Simunek and van Genuchten, 1994)

$$C(\theta) \frac{\partial T_s}{\partial t} = \frac{\partial}{\partial x} \left[\lambda(\theta) \frac{\partial T_s}{\partial x} \right] - C_w q \frac{\partial T_s}{\partial x} \quad [7]$$

where T_s is soil temperature ($^{\circ}K$); $C(\theta)$ and C_w are the volumetric heat capacity for soil and water [$MT^2/(L K)$], respectively; and $\lambda(\theta)$ is the apparent thermal conductivity of the soil [$ML/(T^3 K)$].

To simulate MeBr transport and volatilization, a finite-element computer code, CHAIN_2D by Simunek and van Genuchten (1994), was used to simultaneously solve Eq. [5] to [7]. The initial condition or source for MeBr diffusion was obtained after the early time convective redistribution from the hot-gas injection. The surface boundary flux was described with Eq. [1] for MeBr volatilization through the plastic films and no water evaporation was permitted. Measured air and soil surface temperatures were used as input in Eq. [7] to derive soil temperatures at different depths. While the air temperatures (above and below the film) were used to calculate film permeability, soil temperatures were included in calculating MeBr water-vapor phase partition coefficient or the Henry's constant and its diffusion coefficient in soil air using functional relationships reported in Wang et al. (1997c).

RESULTS AND DISCUSSION

Measured MeBr volatilization from the calibration enclosure exhibited a very strong cyclic behavior (Fig. 2A) synchronous with measured temperature variations of either the chamber air or the air inside the enclosure (Fig. 2B). This indicates that the permeability of the PE film to MeBr may be correlated with temperature changes. The daily maximum flux decreased from $J_M = 310 \mu\text{g}/(\text{m}^2 \text{ s})$ right after MeBr application to $J_M = 54 \mu\text{g}/(\text{m}^2 \text{ s})$ 5 d after application. This is caused by the reduced concentration gradient across the film since MeBr concentration inside the calibration enclosure had decreased from an initial $C_e = 162$ to 23 mg/L during this time span (Fig. 3). Methyl bromide concentration in the air stream of the flux chamber remained very small ($C_a < 0.1 \text{ mg/L}$), insignificant compared to C_e . The difference in air temperature between the chamber and calibration enclosure was very small (Fig. 2B). Therefore, the temperature of the PE film can be accu-

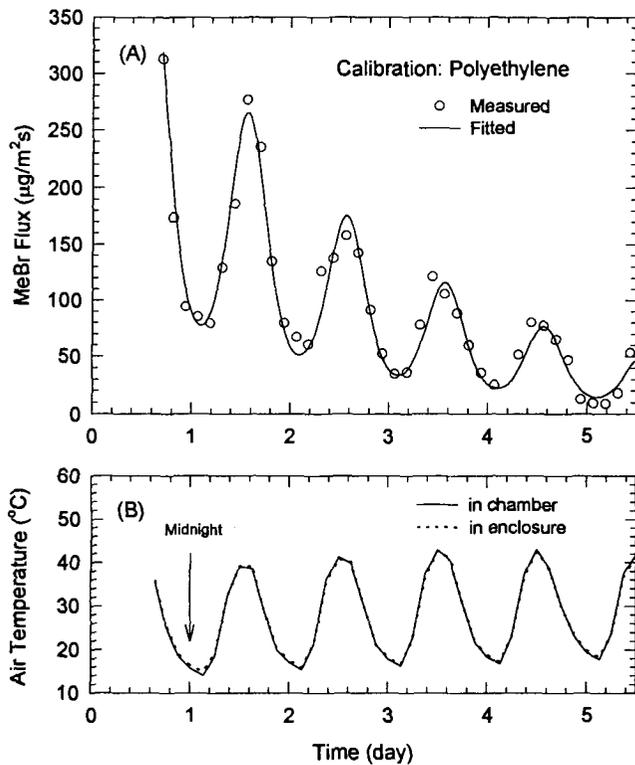


Fig. 2. Calibrating methyl bromide (MeBr) volatilization through the polyethylene film: (A) measured and fitted MeBr volatilization flux; (B) measured air temperature.

rately estimated as the mean of the two temperatures. Based on the measured MeBr volatilization flux (J_M), air temperature (T_a), and concentration difference across the PE film ($C_e - C_a$), the effective boundary layer thickness (d^{Tr}) can be obtained at a reference temperature T_r ($= 20^\circ\text{C}$) along with its activation energy (E_a^d), which were 138.5 cm and -37.8 KJ/mol, respectively. Evidence that these parameters are very reasonable is the accuracy of Eq. [2] in describing the measured volatilization flux (Fig. 2A).

Using the Hytibar film, MeBr volatilization was drastically reduced. The daily maximum flux reached only about $5.6 \mu\text{g}/(\text{m}^2 \text{s})$ after MeBr application (Fig. 4A).

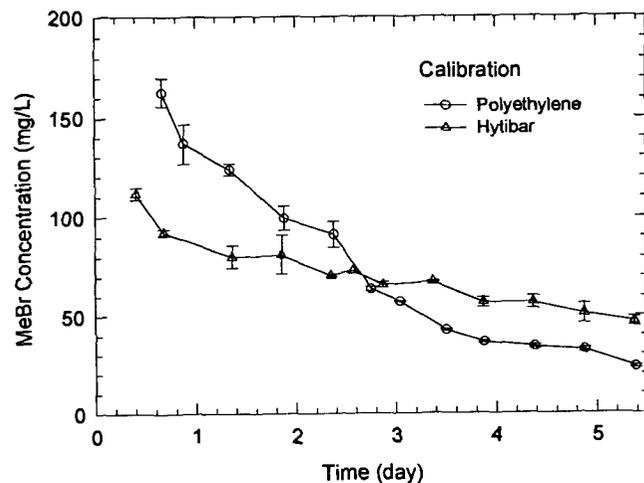


Fig. 3. Methyl bromide (MeBr) concentration in the calibration enclosure when covered with the polyethylene or Hytibar films.

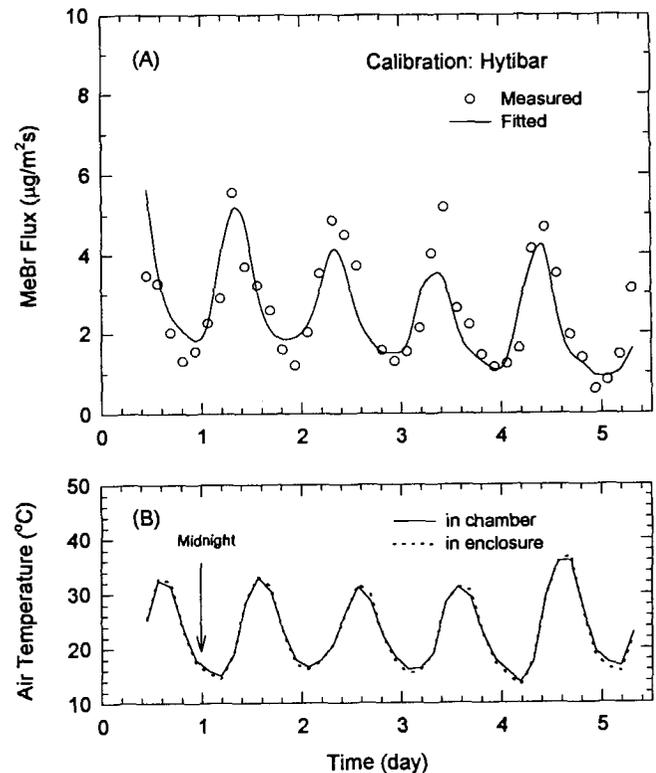


Fig. 4. Calibrating methyl bromide (MeBr) volatilization through the Hytibar film: (A) measured and fitted MeBr volatilization flux; (B) measured air temperature.

Similar to the PE film, MeBr volatilization also exhibited a very strong cyclic behavior synchronous with diurnal air temperature variations (Fig. 4B), and reached a daily maximum near noon and a minimum near midnight. Close examination revealed that the occurrences of maximum and minimum fluxes had a phase lag compared to the timing of measured maximum and minimum air temperatures. This could be caused by changes in thermal properties of the Hytibar film since the additive polymer (i.e., EVOH) could alter the heat capacity and conductivity of the plastic film (Birley and Couzens, 1974). It is also possible that the low permeability would increase the residence time for MeBr molecules to diffuse through the Hytibar film. Therefore, the response time to temperature would be delayed (~ 20 h). Additional study is needed to determine the exact mechanisms causing the phase lag.

The daily maximum flux decreased very slowly and remained at about $4.8 \mu\text{g}/(\text{m}^2 \text{s})$ 4 d after MeBr application (Fig. 4A). This is attributed to the low permeability of the Hytibar film to MeBr gas volatilization. Measurements of MeBr concentration in the calibration enclosure also show that the concentration decreased at a lower rate under the Hytibar than the PE film cover (Fig. 3), indicating the effectiveness of the Hytibar film in containing MeBr gas.

From the measured MeBr volatilization flux (J_M), air temperature (T_a), concentration difference across the film ($C_e - C_a$), and after correcting the phase shift between J_M and T_a , we found that the effective boundary layer thickness (d^{Tr}) at a reference temperature T_r ($= 20^\circ\text{C}$) and its activation energy (E_a^d) for the Hytibar

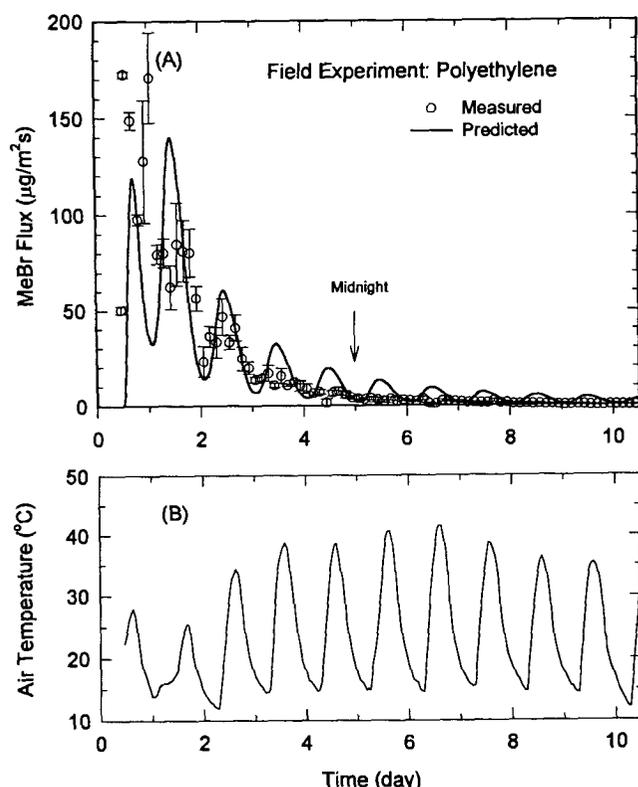


Fig. 5. Measured and predicted methyl bromide (MeBr) volatilization flux density (A) in a field plot covered with the polyethylene film, and measured air temperature (B) at the experimental site.

film were 367.5 m and -43.9 KJ/mol, respectively. While the estimated activation energy for the Hytibar film was similar to that of the PE film, the effective reference boundary layer thickness (d^r) for the Hytibar film was much larger than the PE film (~ 1.4 m).

In the field experiment, variations of measured MeBr volatilization flux from the PE film covered plot appeared to be correlated to diurnal changes in ambient air temperature (Fig. 5A, B), following a pattern similar to observations from the calibration experiment (Fig. 2A). The cyclic behavior was more apparent in the first 4 d after MeBr application when the volatilization flux density was large. Overall, model simulation with parameters estimated independently from the field experiment predicted the volatilization flux and its diurnal cyclic pattern reasonably well (Fig. 5A). Compared to field measurements, model simulation underpredicted the daily maximum fluxes right after MeBr application and overpredicted the maximum fluxes over time. The measured cumulative emission already reached 13% of

the applied amount whereas the prediction was only 3.6% at 6 h (or 0.25 d) after MeBr injection (Table 1). The early time underprediction is probably caused by an inadequate representation of initial convective flow during the pressurized injection. The model simulation considered only diffusion in the soil. The early time convection phase, during the hot-gas injection, was allowed in the model only to modify the initial MeBr concentration distribution as the source for gas diffusion rather than causing direct advective losses. The later-time overprediction is a direct consequence of the early time underprediction since there would be more MeBr remaining in the soil available for further atmospheric volatilization. The overall field-measured emission loss agrees very well with model prediction (about 66–67% of the amount applied in this plot after 10 d, Table 1).

In the field experiment with the Hytibar film cover, measured MeBr volatilization flux never exceeded $3 \mu\text{g}/(\text{m}^2 \text{ s})$ during the experiment and was $<0.5 \mu\text{g}/\text{m}^2 \text{ s}$ after 4 d from the time of MeBr application (Fig. 6A). Measured overall MeBr emission from the Hytibar plot was only 1/35 of that from the PE plot (Table 1). Unlike the calibration experiment (Fig. 4A), the measured MeBr volatilization flux did not seem to correlate with the diurnal air temperature changes (Fig. 6B). It is possible that temperature still affects the permeability of the Hytibar film to MeBr diffusion. However, diffusion and degradation in the soil may play an equal or greater role in controlling MeBr volatilization than the temperature, since the absolute magnitude of emission flux was very small approaching experimental noise range. Except for the first peak, model simulation overpredicted the daily maximum fluxes, artificially created the large diurnal variations (Fig. 6A). The simulation also underpredicted the minimum for the first 3 d after MeBr application. Overall, the model simulation overpredicted MeBr volatilization (15% of applied, Table 1), compared to the measurements (1.9% of applied amount, Table 1). The model overprediction indicates that for an impermeable film such as the Hytibar used under field conditions, other environmental factors may become relatively important in controlling MeBr volatilization since the total emission flux is so small.

In the soil, model simulation predicted the distribution of MeBr gas reasonably well when the plot was covered with the PE film (Fig. 7). The prediction matched the measurements exceptionally well in the 15 to 50 cm depth range. However, the model underpredicted MeBr concentration at 0 to 15 cm and depths below 50 cm for 1 to 5 d after application. The model

Table 1. Methyl bromide volatilization from field plots covered with polyethylene and Hytibar films at selected times after application.

Time	Polyethylene				Hytibar			
	Measured†		Predicted		Measured†		Predicted	
d	g	%	g	%	g	%	g	%
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.25	72 ± 1.2	13 ± 0.2	20	3.6	0.6 ± 0.14	0.1 ± 0.03	0.9	0.2
1	190 ± 1.6	35 ± 0.3	104	19	2.3 ± 0.25	0.5 ± 0.06	3.4	0.8
2	296 ± 23	54 ± 4.1	224	41	4.9 ± 0.04	1.1 ± 0.01	17	4
5	356 ± 34	65 ± 6.2	323	59	7.0 ± 0.05	1.6 ± 0.01	43	10
10	366 ± 36	67 ± 6.6	363	66	7.9 ± 0.18	1.9 ± 0.04	64	15

† SE.

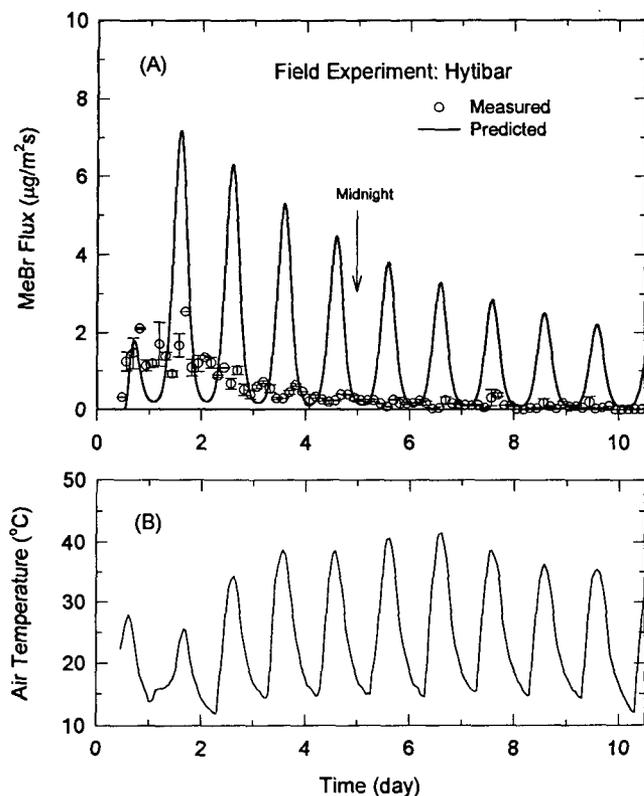


Fig. 6. Measured and predicted methyl bromide (MeBr) volatilization flux density (A) in a field plot covered with the Hytibar film, and measured air temperature (B) at the experimental site.

underprediction of MeBr concentration at early times after application (i.e., 1 or 2 d) and at locations away from the source (i.e., 25 cm) was probably caused by the convective flow created during the pressurized injection. The convective flow mechanism would transport MeBr

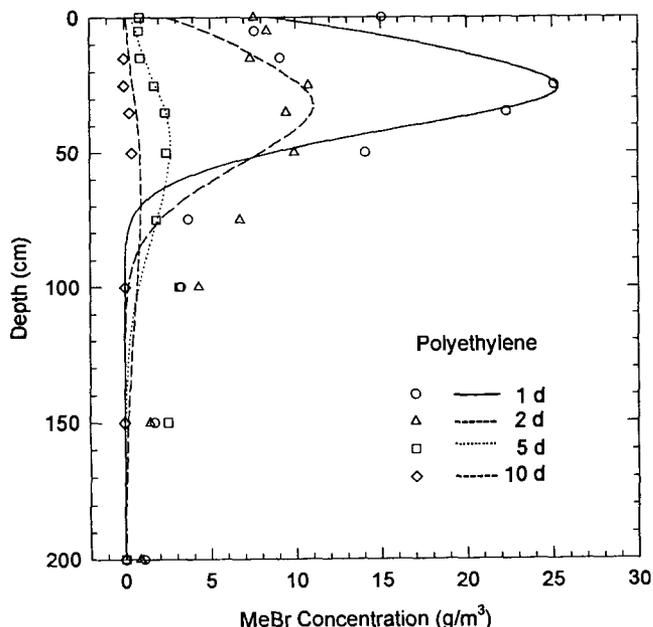


Fig. 7. Measured (symbols) and predicted (lines) methyl bromide (MeBr) concentrations in the soil profile at 1, 2, 5, and 10 d after application when covered with the polyethylene film.

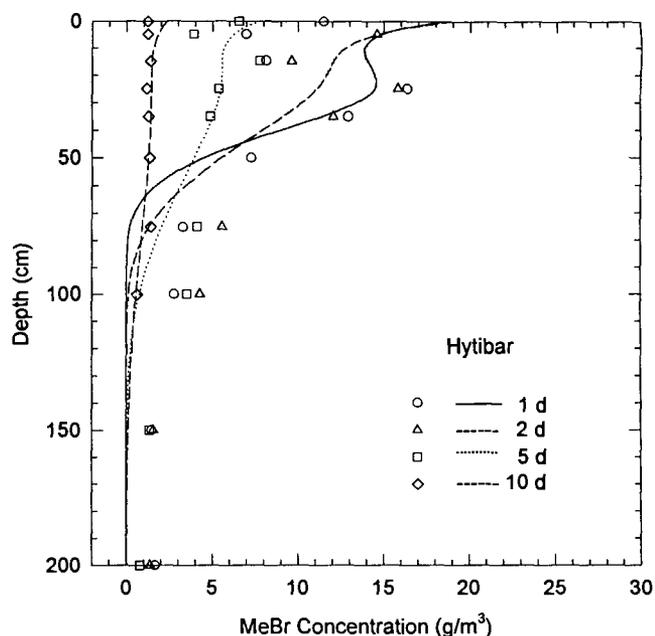


Fig. 8. Measured (symbols) and predicted (lines) methyl bromide (MeBr) concentrations in the soil profile at 1, 2, 5, and 10 d after application when covered with the Hytibar film.

gas to farther distances than the diffusion-type of flow. The slow movement of MeBr gas to deeper depth in the simulation may also be attributed to soil heterogeneity since the soil at depths below 50 cm may have a larger porosity for gas movement and less organic matter content for MeBr retardation than soils near the surface.

In the Hytibar film covered plot (Fig. 8), the measured maximum MeBr gas concentration at 1 d after application was about 16.5 g/m^3 which is much smaller than 25.2 g/m^3 of the PE plot (Fig. 7). The reduced concentration was caused by the lower application rate in the Hytibar plot 21 g/m^2 than in the PE plot (28 g/m^2). Similar to the PE film covered plot, model simulation predicted the distribution of MeBr gas concentration reasonably well. The model simulation underpredicted MeBr concentration at depths below 50 cm for 1 to 5 d after application due to either an underrepresentation of the convective flow or unaccounted changes in soil properties in the model formulation. Unlike in the PE plot, the model overpredicted MeBr concentration at the soil surface or just below the Hytibar film. This may be partially responsible for the model overestimation of the volatilization flux, since the predicted concentration gradient across the Hytibar film would be larger than the actual values (Fig. 6A).

It appears that the model overemphasized the effect of the cover films on MeBr volatilization. Because MeBr was injected in the soil, apparent soil properties pertinent to gas transport such as porosity and water or organic matter content would play an equal or greater part in controlling the fate and movement of MeBr, compared to the films. The effect of soil properties would become more important when a highly impermeable film is used to contain MeBr, because the much reduced emission loss would retain a large fraction of the applied MeBr in the soil, subjecting it to additional

degradation and redistribution. Furthermore, the Hytibar film may require a longer cover period than the PE films since soil degradation may be the only mechanism that MeBr can be eventually removed from the soil-film-air system.

SUMMARY AND CONCLUSIONS

Volatilization of MeBr gas across a PE or Hytibar plastic film was studied from three approaches. First, we obtained the functional relationships between temperature and film permeability to MeBr gas from a calibration study where there was only an air phase at the MeBr source. Then, a field experiment was conducted to determine MeBr volatilization dynamics and total emission under the two different plastic films. Finally, we simulated the transport and fate of MeBr in the soil and volatilization into the atmosphere using a diffusion-based transport model. The model simulation was independent of the field experiment because the input parameters were obtained or estimated from studies not related to this field experiment. The Hytibar film was found to be much less permeable to MeBr than the PE film. This finding implies that, to significantly reduce MeBr emission, the Hytibar film might be used as an alternative to PE films in agricultural fumigation. Methyl bromide emission was found to be strongly affected by temperature changes of either the PE or Hytibar film in the absence of soil. Large volatilization fluxes were observed near noon when the ambient air temperature was high and small fluxes near midnight when the temperature was low. Under field conditions, a diurnal cycling of MeBr volatilization was apparent during the first few days after MeBr application when the absolute MeBr emission flux values were large. At large times, however, the measured emission fluxes appeared to be less cyclic because probably of the much reduced flux density. The temperature effect on MeBr volatilization was less significant for the Hytibar film than for the PE film under field conditions because of the much reduced absolute flux values. Model simulation predicted MeBr volatilization reasonably well for the PE covered field plot, but overpredicted the emission for the Hytibar plot. Predicted MeBr concentration in the soil matched measured values reasonably well, especially near the injection depth. Under- or overprediction was found near the surface or at depths below 50 cm when the soil properties might have changed. Improvement in model simulation can be made by incorporating convective gas flow in the soil and inclusion of soil properties from different depths in the profile.

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