Organic Chemicals in the Environment

Temperature Effect on Methyl Bromide Volatilization in Soil Fumigation

D. Wang,* S. R. Yates, and J. Gan

ABSTRACT

Recent interest in characterizing methyl bromide emission has focused on field and laboratory measurements, which are expensive to conduct and very time consuming. Predicting methyl bromide volatilization with numerical or analytical models has been limited to idealized situations without considering environmental conditions such as diurnal temperature change. It has been found that temperature can strongly affect methyl bromide volatilization under field conditions. To quantitatively characterize temperature effect, we adopted a two-dimensional numerical model that can solve simultaneous equations of water, heat, and solute transport (including both liquid and vapor phases). Functional relationships were established between temperature and methyl bromide liquid-gas phase partition coefficient or the Henry’s constant, diffusion coefficient in soil air space, and the permeability of polyethylene tarp. To test the model, soil properties and boundary conditions from Yates et al. (1996a,b,c) were used. The model prediction was completely independent of the field measurement. The model simulation by considering diurnal variations of soil temperature predicted the cumulative emission that agreed well with the measured flux density. Prediction without considering temperature missed the diurnal nature in emission flux density. Comparable results were also obtained for methyl bromide concentration in the soil profile. The key advantage of this model is its ability of describing diurnal variations in methyl bromide emission flux. Based on the temperature effect on temporal variations of methyl bromide emission, we believe that small sampling intervals are needed to determine the dynamic nature of methyl bromide emission under field conditions, especially during the first 24 h after application.

Methyl bromide is a soil fumigant that moves in the soil predominantly in the gaseous phase. Because of the high vapor pressure (approximately 1420 mm Hg at 20°C), it can very quickly reach the soil surface where emission into the atmosphere occurs. Recent research has indicated that agricultural emission of methyl bromide can contribute to the depletion of stratospheric ozone (Mellouki et al., 1992; Reeves and Penkett, 1993). This has caused great interest in characterizing methyl bromide emission under field conditions. It has been estimated that from 30 to 60% of the applied methyl bromide can escape to the atmosphere under conventional fumigation practices, i.e., covering the field with polyethylene plastic film after injecting methyl bromide at about the 25-cm depth (Majewski et al., 1995; Yagi et al., 1993, 1995; Yates et al., 1996a).

Field quantification of methyl bromide emission has been made with either area-weighted micrometeorological approaches such as the aerodynamic, theoretical profile, and integrated horizontal flux methods (Majewski et al., 1995; Yates et al., 1996b) or localized flux chamber methods (Yagi et al., 1993, 1995; Yates et al., 1996a).

When continuous measurements were made at small time intervals such as the study by Majewski et al. (1995) and Yates et al. (1996a,b,c), the methyl bromide emission flux density exhibited a diurnal cycle with the highest flux occurring between midday to early afternoon (or near solar noon). When infrequent measurements were made at about the same time of each day, the flux density was not found to be strongly cyclic (Yagi et al., 1993, 1995). Majewski et al. (1995) and Yates et al. (1996a,b,c) accredited the cyclic behavior in emission rate to diurnal changes in solar energy and atmospheric stability. Besides solar energy and atmospheric stability, the fate and transport of a volatile organic chemical such as methyl bromide is strongly influenced by many variables including chemical partitioning between soil water and air phases characterized by the Henry’s constant, its effective vapor diffusion coefficient, adsorption to soil particles, and degradation rate. Past and present modeling efforts on methyl bromide fate and transport in the soil have assumed constant values for these transport parameters (Rolston and Glauz, 1982; Reible, 1994) without considering the important diurnal changes in surface energy exchange between soil surface and the atmosphere. These simplified approaches, though they may still be able to reproduce an average flux rate and overall emission that are comparable to measured values (assuming continuous cumulative measurements), often result in mismatches between the predicted and measured flux density of methyl bromide emission for different times during a daily cycle.

Volatilization of a vapor-phase organic compound such as methyl bromide can be estimated with the inclusion of physical and chemical parameters that control its concentration at the soil surface (Spencer et al., 1982). In fact, the volatility of a chemical may increase three to four times for each 10°C increase in temperature (Taylor and Spencer, 1990). Besides the direct effect on chemical properties, temperature can also affect the permeability of plastic films that are used to cover the fumigated fields. An increase in flux density through the polyethylene plastic film, when temperature increases, has been observed by Kolbezen and Abu-El-Haj (1977). Yates et al. (1996c) consequently estimated methyl bromide emission flux based on flux chamber measurements after accounting for the temperature dependency of plastic film permeability. From a modeling standpoint, energy exchange between soil and the atmosphere would result in diurnal variations in soil temperature. The partition ratio between soil water and air phases and effective vapor diffusion coefficient would be affected by temperature changes, while the adsorption to soil particles and degradation rate would also be likely temperature-dependent, though maybe to a lesser degree. Therefore, in field situations these parameters are both temporally and spatially dependent. The other fac-
The purpose of this study was to investigate the temperature effect on methyl bromide emission. This was achieved by adopting a numerical model that can simultaneously solve the partial differential equations for heat, water, and vapor transfer. Functional relationships were established between soil temperature and methyl bromide diffusion coefficient, the Henry's constant, and the permeability of a polyethylene tarp. The simulation result was compared with a field experiment reported by Schwarzenbach et al. (1993), which functions as a carrier for methyl bromide transport in the soil. To simulate methyl bromide fate and transport under actual field conditions, a comprehensive two-dimensional finite element model, CHAIN_2D (Simunek and van Genuchten, 1994), was made in comparing with the experimental results.

The expression used in the simulation model for temperature-dependent variables is the Arrhenius equation and it used for solutes in liquid and solid phases. For a volatile organic chemical such as methyl bromide, the governing transport for solutes in liquid and solid phases is the diffusion in water.

The diffusion coefficient of methyl bromide is 0.1037 (cm²/s), which is within the range of reported diffusion coefficients for methyl bromide (Dw) is 1.35 x 10⁻⁵ (cm²/s), which is about 10,000 times smaller than the diffusion coefficient in 25°C water (Dg). Since methyl bromide diffusion in water was considered using a constant diffusion coefficient, i.e., Dw = 1.35 x 10⁻⁵ (cm²/s) at 25°C. A more than Dg (Maharajh and Walkley, 1973). Since methyl bromide diffusion (Dw) is 1.35 x 10⁻⁵ (cm²/s), which is about 10,000 times smaller than the diffusion coefficient in 25°C water (Dg).

The diffusion coefficient in 25°C water was determined with a semi-empirical equation developed by Jin and Jury (1995; Reible, 1994; Rolston and Glauz, 1982).

\[ D_g = \frac{0.0323 \times T}{1000^{1.75}} \times \frac{1}{10^{7.37 \times 10^{-5}}} \]

This equation is reasonable because the estimated Dg at 20°C is 0.2038.

Energy required for the methyl bromide diffusion coefficient, i.e., Dw = 1.35 x 10⁻⁵ (cm²/s) at 25°C. A more than Dg (Maharajh and Walkley, 1973). Since methyl bromide diffusion (Dw) is 1.35 x 10⁻⁵ (cm²/s), which is about 10,000 times smaller than the diffusion coefficient in 25°C water (Dg).

The temperature dependency of methyl bromide diffusion coefficient can be written as (Simunek and van Genuchten, 1994):

\[ D_g = \frac{0.0323 \times T}{1000^{1.75}} \times \frac{1}{10^{7.37 \times 10^{-5}}} \]

The activation energy for the methyl bromide diffusion coefficient is 0.1037 (cm²/s), which is within the range of reported diffusion coefficients for methyl bromide in water (Dw) is 1.35 x 10⁻⁵ (cm²/s), which is about 10,000 times smaller than the diffusion coefficient in 25°C water (Dg).

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The individual components of $D_{ij}$ in the soil matrix for two-dimensional transport are:

$$D_{xx} = D_L q_{xx} + D_T q_{xz} + D_{wr} w + a_s K_h D_g g$$  \[9a\]

$$D_{zz} = D_L I - I q_{zt} + D_{gw} g$$  \[9b\]

$$D_{xz} = (D_I - D_T) q_{xz}$$  \[9c\]

where $D_L$ and $D_T$ are the longitudinal and transverse dispersivities; $q_{xx}$ and $q_{zz}$ are the components of the Darcian fluid flux density; $D_g$ and $D_w$ are the molecular diffusion coefficients in water and air; and $w$ and $g$ are tortuosity factors for the liquid and gaseous phases, respectively. While $w$ was calculated from the widely used Millington-Quirk equation (Millington and Quirk, 1960):

$$w = \frac{\eta_{air}}{\eta_{water}}$$  \[10\]

where $\eta$ is soil porosity, and $g$ was calculated from:

$$g = \frac{\eta_{air}}{\eta_{water}}$$  \[11\]

which can also be found in Millington and Quirk (1960).

Used Eq. \[11\] instead of Eq. \[10\] because Jin and Jury (1996) concluded that Eq. \[11\] was more suitable for gas phase diffusion than Eq. \[10\], based on their laboratory experimental results.

**Boundary Conditions**

A volatilization boundary condition is implemented in CHAIN_2D using an equation of the form

$$h(C_g - C_{atm})$$  \[12\]

where $h$ is a mass transfer coefficient and $C_{atm}$ is the gas concentration above the boundary layer. In CHAIN_2D, $h$ is the only adjustable parameter for characterizing the resistance (i.e., $1/h$) to transport across the soil-atmosphere interface. Since with a tarped system there are several resistances affecting gas movement from the soil into the atmosphere, to utilize CHAIN_2D, these have to be written as a single effective resistance.

A more complete mathematical description for the boundary layer as shown in Fig. 1 would be

$$h_1(C_g - C_{atm, b}) + h_2(C_{atm, b} - C_{atm, t}) + h_3(C_{atm, t} - farm)$$  \[13\]

where $h_1$, $h_2$, and $h_3$ are the mass transport coefficients, respectively, between the soil and underside of the tarp, between the underside and top of the tarp and between the tarp surface and the atmosphere; and $C_{atm, b}$ and $C_{atm, t}$ are concentrations at underside and top of the tarp.

Under field conditions, the space between the soil surface and the plastic tarp will vary spatially due to the unevenness of the soil surface microrelief. Changes in wind speed over the tarp would also constantly alter this spacing, the vertical flapping of the tarp by the wind, along with molecular diffusion, would constantly mix the methyl bromide so that it would be reasonable to assume a uniform concentration within this air space (i.e., $C_g = C_{atm, b}$). Therefore, the difference in the first term on the right-hand side of Eq. \[13\] approaches 0. Since the remaining terms are not zero, we write them as

$$h(C_g - C_{atm}) = h_2(C_{atm, b} - C_{atm, t}) + h_3(C_{atm, t} - farm)$$  \[14\]

Once $h = D_g/\rho$ is determined, CHAIN_2D can be used to simulate the volatilization process.

To estimate the effective boundary layer resistance, we first considered the tarp resistance to methyl bromide diffusion, i.e., the $1/h_2$ term. From Yates et al. (1996b), we estimated $h_2$ to range from 0.000623 to 0.00506 (cm/s) for tarp temperatures between 24 to 60°C. The tarp resistance would be between 160 to 514 and 19763 (s/m). For the same temperature range, $D_g$ changes from 0.106 to 0.233 (cm²/s) according to Eq. \[6\]. This would provide a boundary layer thickness induced by the tarp resistance or $d_2$ ranging from 170 to 46 (cm).

To include the temperature dependency of the tarp resistance in the simulation, we further found the activation energy for $d_2$: $E_{act} = -3.3166 \times 10^{-1}$ (J/mol) for $T_{air} = 20°C$ and $d_2 = 191.64$ (cm).

To determine the transfer coefficient between the tarp surface to the atmosphere or $h_3$, we used a resistance analogue similar to Baker et al. (1996), where the overall resistance (or $1/h_3$) consisted of a diffusive ($r_a$) and an aerodynamic ($r_{a,h}$) component, i.e., $r_3 = r_a + r_{a,h}$, where

$$Re;4Scm \\ r_a = \frac{u^2}{u_h} \\ r_{a,h} = \frac{Re;4Scm}{Re;4Scm}$$  \[15a, b\]
Yates et al., 1996a). Because the field was covered with plastic film (Yates et al., 1996a), the surface was aerodynamically smoother than either a bare or vegetative surface cover. The initial concentration for two-dimensional diffusion with a continuous source from a depth range was given by:

\[ \text{CL}_{g}(\bar{x}, Z, 0) = \text{Co}(\bar{x}, \bar{z}) \]  

When comparing the field experimental results from Yates et al. (1996a,b,c), Eq. [19a] and [19b] were used with \( \bar{z} = 24.45 \) cm, \( \bar{z} = 25.45 \) cm, and \( \text{Co}(\bar{z} \rightarrow Z \rightarrow \bar{z}) = 1.7 \text{ mg/cm}^3 \) which represents the resistance to methyl bromide volatilization after tarp removal. This is a reasonable number for bare soil surface conditions as:

\[ \text{Re}, = 0.1, \frac{\partial}{\partial Z} \frac{\partial}{\partial \bar{x}} \text{Dg}(T) \]  

where \( h_2 \) can be described in CHAIN_2D model as:

\[ h_2 = \text{Re}_{10} = 0.1. \]

Because the tarp was removed at 5.029 d after application, tarp removal. This is a reasonable number for bare soil surface condition as:

\[ h_2 = \text{Re}_{10} = 0.1. \]

The initial concentration for one-dimensional diffusion with a line source was given by:

\[ \text{CL}_{g}(X, Z, 0) = 0 \]  

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Table 1. Soil physical, chemical, and hydraulic properties used in model simulation.

<table>
<thead>
<tr>
<th>Layer Depth</th>
<th>Bulk Density (g/cm³)</th>
<th>Water Adsorption Rate (cm³/g)</th>
<th>Degradation Rate (cm ¹/g)</th>
<th>Initial Water Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-5.2</td>
<td>1.30</td>
<td>0.12</td>
<td>0.0791</td>
<td>1100</td>
</tr>
<tr>
<td>5.2-10</td>
<td>1.43</td>
<td>0.12</td>
<td>0.0791</td>
<td>1100</td>
</tr>
<tr>
<td>10-20.5</td>
<td>1.55</td>
<td>0.15</td>
<td>0.0791</td>
<td>450</td>
</tr>
<tr>
<td>20.5-30.2</td>
<td>1.65</td>
<td>0.18</td>
<td>0.0899</td>
<td>425</td>
</tr>
<tr>
<td>30.2-40</td>
<td>1.65</td>
<td>0.20</td>
<td>0.0899</td>
<td>280</td>
</tr>
<tr>
<td>40-50</td>
<td>1.65</td>
<td>0.22</td>
<td>0.1026</td>
<td>130</td>
</tr>
<tr>
<td>50-60</td>
<td>1.65</td>
<td>0.21</td>
<td>0.1026</td>
<td>165</td>
</tr>
<tr>
<td>60-80</td>
<td>1.65</td>
<td>0.20</td>
<td>0.0775</td>
<td>850</td>
</tr>
<tr>
<td>80-100</td>
<td>1.65</td>
<td>0.20</td>
<td>0.0798</td>
<td>680</td>
</tr>
<tr>
<td>100-1000</td>
<td>1.65</td>
<td>0.20</td>
<td>0.0000</td>
<td>4900</td>
</tr>
</tbody>
</table>


Ganet al. (1994), degradation occurs in liquid and solid phases, not in gaseous phase.

\( a \) and \( n \) are fitted parameters.

The cumulative amount of methyl bromide emission followed the same trend with or without considering temperature effect (Fig. 2B). However, because of the cyclic nature in flux density the accumulation rate followed a similar pattern to the diurnal changes in emission flux, whereas that without temperature effect was a smooth curve. After 5.029 d (before tarp removal of Yates et al., 1996c), 53.4% of the applied mass was lost via emission. This is comparable to the measurement by Yates et al. (1996b,c) where 54.9 to 65.1% was considered to be lost by volatilization before tarp removal.

Fig. 2. (A) Simulated methyl bromide flux density and (B) cumulative mass loss with the inclusion and exclusion of diurnal temperature variations under the tarp with \( T_o = 40°C \) and \( \Delta T = 22°C \).

If the volatilization rate was measured only once a day, say at 1200 h, and using this rate to represent that day's emission flux, the cumulative emission at 5.029 d after application would be 88.9%. This is clearly an overestimation of the actual emission rate.

Simulated methyl bromide flux matched the measured values reasonably well and both followed a diurnal variation with high fluxes occurring between noon and early afternoon hours of each day and low values around midnight to early morning (Fig. 3). The measured peak flux values of 118.9, 110.6, and 61.3 (µg/m² s) at 1.01, 1.72, and 2.80 d did not follow the simulation and may be attributed from other factors such as barometric pressure changes or atmospheric instability, which cannot be simulated using CHAIN_2D. The model simulation may be improved by incorporating the barometric pressure and atmospheric instability effect. The disadvantage for including the barometric pressure and atmospheric instability is that actual field measurement is required, which renders the model prediction not completely independent of field measurement, therefore limiting its use.

We used the flux values from the chamber measurement, i.e., Yates et al. (1996c), to compare with the model prediction because these flux estimates have been corrected for temperature effect on the polyethylene plastic tarp. We believe that the increased methyl bromide diffusion coefficient, with increasing temperature, would contribute to a significant portion of the flux enhancement factor reported in Yates et al. (1996c).

According to Eq. [6], methyl bromide diffusion coefficient will increase by 20% when increasing temperature from 10 to 40°C, whereas the temperature enhancement factor would double in every 15°C increase. According to Eq. [12], the increased diffusion coefficient would lead to increased emission flux values assuming other parameters or variables unchanged. The major effect of temperature on the flux enhancement factor may be attributed to the increased permeability to methyl bromide molecules due to thermal expansion or other physiochemical mechanisms of the plastics (Birley and Couzens, 1974). This effect can be seen by comparing the simulated emissions when fixing the boundary layer
Table 2. Methyl bromide partition between emitted, degraded, and remained in the soil at selected times after injection.

<table>
<thead>
<tr>
<th>Elapsed time (d)</th>
<th>dc =</th>
<th>dc or</th>
<th>dc or</th>
<th>dc or</th>
<th>dc or</th>
<th>dc or</th>
<th>dc or</th>
<th>dc or</th>
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<th>dc or</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>100.0</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>0.04167 (= 1 h)</td>
<td>1.1</td>
<td>1.3</td>
<td>1.4</td>
<td>11.7</td>
<td>1.8</td>
<td>1.7</td>
<td>98.5</td>
<td>98.3</td>
<td>1.4</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>0.2083 (=5 h)</td>
<td>1.9</td>
<td>5.4</td>
<td>6.3</td>
<td>24.0</td>
<td>3.5</td>
<td>3.3</td>
<td>95.8</td>
<td>92.5</td>
<td>1.2</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>0.4167 (=10 h)</td>
<td>0.96211.9</td>
<td>17.3</td>
<td>23.0</td>
<td>42.3</td>
<td>7.5</td>
<td>7.2</td>
<td>81.8</td>
<td>76.6</td>
<td>1.2</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>0.96243.029</td>
<td>0.2083</td>
<td>1.3</td>
<td>1.0</td>
<td>52.5</td>
<td>13.5</td>
<td>12.7</td>
<td>57.3</td>
<td>52.0</td>
<td>1.3</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>1.0295.029 (tarp off)</td>
<td>0.4167</td>
<td>1.9</td>
<td>5.4</td>
<td>24.0</td>
<td>3.5</td>
<td>3.3</td>
<td>95.8</td>
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<td>81.8</td>
<td>76.6</td>
<td>1.2</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

dc = 122.6 cm before tarp removal; dr = 34.8-210.4 cm before tarp removal; dc or T = dB = 0.5 cm after tarp removal (t > 5.029 d).

Data from Yates et al. (1996b,c) of aerodynamic, theoretical profile shape, integrated horizontal flux, and the flux chamber methods. The were referencing that measured at 0.229 d after application. The 18.129 and 35.029 d data were referencing measurements up to 14.342 further emission had been observed for 6 d.

Despite the predicted overall emission (53.4% after 5.029 d) being similar to that from the meteorological and chamber methods (54.9-65.1%; Yates et al., 1996b,c), the predicted flux density was not as variable as that estimated from the meteorological approaches, in which the flux fluctuated between about 4 to 786 (mg/m² s) within 12 h such as in the theoretical profile shape method. The large variability in measured emission flux was caused by atmospheric instability and experimental error. While the model prediction is useful in describing the basic principles in transport and volatilization processes to the accuracy of our current understanding, experimental measurements provide outcomes that include all relevant processes taking place and are very important in validating the simulated mechanisms such as the temperature effect.

A potential application of understanding the temperature effect on diurnal fluctuations in methyl bromide volatilization is to schedule sampling times so that more representative emission rates can be obtained. Because the temporal distribution of methyl bromide emission appeared to follow a diurnal sine wave with its mean fitting to a lognormal distribution (Fig. 2 and 3), believe that multiple samples are necessary during the first 24 h after application. Over time, a single sample may be enough for each day if it is taken near the mean. However, a representative daily mean emission rate is difficult to determine because we do not fully understand all the important processes such as barometric pressure and atmospheric instability that would affect the volatilization mechanisms. Therefore, we recommend high-frequency sampling, whenever possible. Above implications to sampling apply to places where discrete samples are taken at selected times or days after application such as in Yagi et al. (1993). It will not be a concern if the sampling is made continuously such as in Majewski et al. (1995) and Yates et al. (1996a,b,c).

Methyl bromide concentration in the soil air redistributed quickly after injection at 25 cm. Both simulated and measured concentration values at selected times after application showed the rapid redistribution process. The simulation predicted the measured values reasonably except at deeper depths (Fig. 4). The discrepancy may also be caused by downward mass flow caused by density sinking. Density sinking of methyl bromide (Goring, 1962) is simply caused by the fact that methyl bromide (3.974 mg/cm³) is heavier than soil air (~1.18 mg/cm³). Therefore, at early times, the local gas phase density of the air containing methyl bromide is greater than the surrounding methyl bromide free air phases and this density difference produces an advective mass flow. Other factors that might have contributed to methyl bromide transport included a potential preference upward movement above the injection lines. This is possible since preferential paths could be created because methyl bromide was injected through a shank that would create a fracture connecting the source to the soil surface. Although the soil would fall back to close...
Fig. 4. Comparison of simulated and measured methyl bromide concentrations in the soil profile at 1.4, 2.5, 4.4, 5.5, 18.6, and 35.5 d after application. The measured values were from Yates et al. (1996a).

The shank fracture, the soil directly above the injected methyl bromide, would be less compacted than the rest of the profile and could provide a preferred transport pathway. Therefore, there was a potential for a preferred transport through the shank fractures. The preferential flow would play a more significant role in the early stages of redistribution when pressure-driven flow dominated and may be a mechanism causing the high fluxes almost immediately after the application as observed in recent field experiments (Majewski et al., 1995; Yates et al., 1996b). Because methyl bromide was injected as a liquid, it would vaporize very rapidly (boiling point = 3.56°C) under ambient temperatures. The initial phase-change expansion would increase the absolute pressure of methyl bromide gas near the source creating an advective or pressure-driven flow. This would help to disperse methyl bromide very quickly. After this initial stage, gas-phase diffusion would be the main mechanism for spreading methyl bromide in the soil matrix, which is driven by concentration gradient. The presence of plastic tarp would help to contain the gas near the soil surface.

From a model simulation, additional information is available about the quantities of methyl bromide emitted, degraded and remaining in the soil any time after application. This is a very useful feature because it would help to determine the actual exposure time under some threshold concentration to achieve efficient efficacy. It would also help to decide the duration of the fumigation and the dosage to apply. While the diffusion rate is strongly affected by the diffusion coefficient, which is, besides temperature, also a function of soil air content. It is a common practice in agricultural fumigation to minimize soil moisture content before injection to increase soil aeration. Adsorption and degradation rate, however, are more generic to the soil to be treated. Gan et al. (1994) indicates that both the adsorption and the degradation rate are strongly dependent on soil organic matter content. While adsorption would not remove methyl bromide from the soil profile, degradation would irreversibly eliminate it from the soil. Therefore, soils with high degradation rate or high organic matter content may require larger application dosage than soils with low organic matter content. The other way for methyl bromide to reduce to mineral forms is by hydrolysis or reacting with water. Therefore, managing soil moisture content before methyl bromide injection would not only help to achieve a reasonable dispersion rate but could affect degradation rate. With the model, soil moisture content or air porosity can potentially be optimized. In summary, improvements that we can make to the simulation model are to include barometric pressure changes at the soil surface, initial stage pressure-driven flow, density-driven flow, and preferential flow through the shank traces. In future modeling activities, we should also include the temperature dependency of tarp permeability through plastic films of different composition such as the Hytibar (Daponte, 1995) as compared with the conventional polyethylene films.

CONCLUSIONS

Diurnal variations in methyl bromide volatilization flux were simulated with a two-dimensional numerical model by solving simultaneous equations of water, heat, and solute transport (in both liquid and vapor phases). This was achieved by establishing functional relationships between temperature and methyl bromide Henry’s constant, diffusion coefficient in air, and tarp permeability. Soil properties and surface boundary conditions from Yates et al. (1996a,b,c) were used as an example for model comparison. The model depicted diurnal changes in methyl bromide emission flux density comparable to the measurements by Yates et al. (1996c). Simulated methyl bromide concentration distributions in the soil profile matched the measurements reasonably well. The model may be improved by including atmospheric barometric pressure variations, early time pressure-driven advective flow and density-driven flow.