

Methyl Bromide Emissions from a Covered Field: II. Volatilization

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ABSTRACT

An experiment to investigate the environmental fate and transport of methyl bromide in agricultural fields is described. The methyl bromide volatilization rate was determined as a function of time for conditions where methyl bromide was applied at a rate of 843 kg in a 3.5-ha (i.e., 240 kg/ha) field covered with plastic at a depth of 25 cm. Three methods were used to estimate the methyl bromide volatilization rate, including: the aerodynamic, theoretical profile shape and integrated horizontal flux methods. The highest methyl bromide volatilization rates were at the beginning of the experiment. Within the first 24 h, approximately 36% of the applied methyl bromide mass was lost. Diurnally, the largest volatilization rates occurred during the day when temperatures were high and the atmosphere was unstable. Cooler temperatures, light winds, and neutral to stable atmospheric conditions were present at night, reducing the flux. The total emission calculated using these methods was found to be approximately 64% ($\pm 10\%$) of the applied mass. A mass balance was calculated using each flux estimation technique and several methods for analyzing the data. The average mass recovery using all the flux methods was 867 kg (± 83 kg), which was 102.8% ($\pm 9.8\%$) of the applied mass (i.e., 843 kg). The range in the mass balance percent (i.e., percent of applied mass that is measured) is from 88 to 112%. The averaged mass balance percent for the aerodynamic method, which involved using the measured data directly, was approximately 100.8%. The total emission calculated using the aerodynamic method was found to be approximately 62% ($\pm 11\%$) of the applied mass.

METHYL BROMIDE has been used for decades as a soil fumigant for the control of nematodes, weeds, and fungi and has recently come under scrutiny as a chemical that depletes stratospheric ozone. As a result of the Clean Air Act, methyl bromide is scheduled for phase-out by the year 2001. The USDA National Agricul-

tural Pesticide Impact Assessment Program has completed an assessment of methyl bromide and determined that there will be substantial adverse economic impacts on the agricultural community if the use of methyl bromide is restricted.

Much of the concern for using methyl bromide for agricultural fumigation results from its high vapor pressure (1420 mm Hg at 20°C). Vapor diffusion plays a predominant role in the spreading of methyl bromide throughout the soil profile and in controlling pests (Goring, 1962; Kolbezen et al., 1974). When injected into the soil, compounds with a high vapor pressure can diffuse to the soil surface and escape into the atmosphere. It has been long established that volatilization is an important pathway for loss of organic chemicals with moderately high vapor pressures from land surfaces (Taylor, 1978; Cliath et al., 1980), and is a major mechanism affecting transport to the atmosphere for highly volatile pesticides such as methyl bromide (Reible, 1994; Yagi et al., 1993). Volatilization of organic chemicals during their use, or following the disposal of waste or consumable goods containing the chemical, is an important source of organic pollutants to the atmosphere.

Volatilization of chemicals from soils can be estimated from a consideration of the physical and chemical factors controlling their concentration at the soil surface (Spencer et al., 1982). When an organic chemical is mixed into the soil, the volatilization rate depends on complex interactions between the sorbed, liquid and vapor phases, movement of the liquid, interactions between the liquid and soil-gas phases, movement from vapor diffusion, and advection as well as other external processes such as energy-induced movement (i.e., induced from heating, barometric pressure, or surface wind), diffusion through a surface boundary layer, turbulent transfer in the atmosphere, etc.

Soil-incorporated chemicals volatilize at a rate dependent on three major factors: (i) their effective vapor

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pressure within the soil, (ii) their rate of movement to the vaporizing surface, and (iii) their rate of movement away from the surface through the air boundary layer. Vapor density of a chemical in soil is a reflection of its inherent vapor pressure, its water solubility, and its adsorption to the soil. Vapor density of organic chemicals can be greatly decreased by their interactions with the soil, mainly adsorption. Temperature effects are also important, and increases in volatility of about three to four times for each 10°C increase in temperature have been observed (Taylor and Spencer, 1990).

Methyl bromide forms a highly concentrated gas in the region around the injection point. Vapor diffusion causes the gas to move throughout the soil profile, effectively increasing the treated region from the surface to as much as several meters deep. At normal temperatures and pressure that occur in the field, methyl bromide is a gas; therefore, one common management strategy is to place plastic on the soil surface to reduce the amount of methyl bromide that leaves the soil profile through diffusion and volatilization. There are many different types of plastic material that can be used to inhibit vapor movement into the atmosphere; probably the most commonly used is a 0.025-mm (1-mil) high-density polyethylene film. Plastic covers tend to reduce the amount of material volatilized by blocking the direct passage from the soil to the atmosphere. This may be particularly effective in stopping advective movement due to perturbations in the barometric pressure and from wind effects. However, the plastic material commonly used in agricultural fields is relatively permeable to methyl bromide (Kolbezen and Abu-El-Haj, 1977). Therefore, even when plastics are used, a significant fraction of the applied material can escape the soil zone and enter the atmosphere. For example, in a field near Monterey, CA, Majewski et al. (1995) found that when plastic is not used as a cover and methyl bromide is injected at shallow depth, nearly all the applied methyl bromide leaves the treated soil zone after a few days, whereas only about 36% is lost when a plastic is present. For a similar experiment, Yates et al. (1996) found that the total emissions obtained from an estimate of methyl bromide degradation was approximately 61% of the applied methyl bromide. This value is for drier and warmer weather conditions compared with Majewski et al. (1995). Yagi et al. (1993, 1995) found that 34 to 87% of the applied methyl bromide can escape through plastic films.

The spatial distribution in the soil profile and the total amount of methyl bromide that escapes into the atmosphere depends strongly on the soil and hydraulic properties in the subsurface. The relationship between water content and the available air porosity is one of the primary factors controlling the diffusion of methyl bromide (Goring, 1962; Kolbezen et al., 1974; Siebering and Leistra, 1978) in the subsurface. If the water content is very high, thus reducing the air porosity, diffusion occurs primarily in the liquid phase, where it is about four orders of magnitude lower than diffusion in the air phase (Kolbezen et al., 1974; Jury et al., 1983). Increasing the soil water content at the soil surface has been

suggested as a possible mechanism for reducing volatilization into the atmosphere (Reible, 1994; Jin and Jury, unpublished data).

Because of the uncertainty in quantifying environmental fate and transport of methyl bromide (UNEP, 1992), and restricting methyl bromide use will have severe consequences on agriculture in the USA (USDA-NAPIAP, 1993), a research project was initiated to determine the extent of methyl bromide volatilization into the atmosphere. The objective of this article is to describe the methods that were used to estimate the methyl bromide flux into the atmosphere and to describe the results from a recent field experiment conducted to determine the dynamics of the methyl bromide volatilization rate when methyl bromide is applied at a shallow depth under a 0.025-mm (1-mil) polyethylene plastic. Attempts were made to completely investigate the fate and transport of methyl bromide so that a clear picture of the methyl bromide movement and transformation could be obtained. A significant difference between this experiment and previous experiments measuring methyl bromide flux is the inclusion of multiple methods for estimating the emission rate and a mass balance, although more recent experiments have attempted to include mass balance information (Yagi et al., 1995). Without this vital information, it becomes impossible to determine the accuracy of the measured flux.

MATERIALS AND METHODS

The experiment was conducted at the University of California's Moreno Valley Field Station on Field G7, a 4-ha field located in the eastern portion of the station, between 26 Aug. 1993 and 13 Sept. 1993. A complete description of the experimental design, the weather conditions, monitoring of atmospheric and soil gas concentrations, methyl bromide degradation in soil, and an estimate of total emission to the atmosphere using methyl bromide degradation and mass remaining in the soil is given by Yates et al. (1996).

Three methods based on atmospheric measurements of methyl bromide were used to obtain experimental values for the rate of volatilization of methyl bromide as a function of time when the soil surface covered with a plastic: the aerodynamic, theoretical profile shape, and integrated horizontal flux methods.

Aerodynamic Method

The aerodynamic method uses atmospheric gradients of the wind speed, temperature, and concentration to provide a measurement of the pesticide flux from the soil surface (Parmele et al., 1972; Brutsaert, 1982; Majewski et al., 1989). The method requires a spatially uniform source and a relatively large upwind fetch so that the atmospheric gradients are fully developed. The fetch requirements are generally assumed to be from 50 to 100 times the height of the instruments—for this field, approximately 0.5 to 1.0 m in height.

The aerodynamic method was originally developed for use under neutral atmospheric conditions. Using empirical relations, however, the method can be extended to stable and unstable atmospheric conditions. Numerous stability corrections have been proposed (Fleagle and Businger, 1980; Brutsaert, 1982; Rosenberg et al., 1983). The aerodynamic equa-

tion, suitable for general atmospheric stability conditions, is

$$f_z(0, t) = k^2 \frac{[\bar{c}_1(t) - \bar{c}_2(t)] [\bar{u}_2(t) - \bar{u}_1(t)]}{\varphi_m(t) \varphi_c(t) \ln(z_2/z_1)^2} \quad [1]$$

where $f_z(0, t)$ is the interval-averaged vertical flux at the soil surface, $\bar{u}(t)$ is the interval-averaged wind speed (m/s), z is height above the soil surface (m) (note: $z_2 > z_1$) and $\bar{c}_1(t)$ is the interval-averaged concentration [$\mu\text{g}/\text{m}^3$] at height z_1 above the soil surface. The gradient-based stability corrections for a particular time interval, t , are (Rosenberg et al., 1983)

$$\begin{aligned} \varphi_c = \varphi_m &= (1 - 16 R_i)^{-1/3} & R_i < 0 & \text{unstable} \\ \varphi_c = \varphi_m &= (1 + 16 R_i)^{+1/3} & R_i > 0 & \text{stable} \end{aligned}$$

where it is assumed that the stability functions for momentum and the concentration are the same. The Richardson number, R_i , is

$$R_i = \frac{g}{T} \frac{\partial T}{\partial z} \left[\frac{\partial u}{\partial z} \right]^{-2} \quad [3]$$

where $k \approx 0.4$ is von Kármán's constant, g is the gravitational acceleration (i.e., 9.8 m/s^2) and $T(t)$ is the absolute temperature (K). The gradient Richardson's number is one means for characterizing the importance of buoyancy and mechanical mixing on the turbulence.

Theoretical Profile Shape Method

The theoretical profile shape (TPS) method, described by Wilson et al. (1982), can be used to determine the gaseous mass transfer from field experiments conducted on a circular plot. The TPS method has advantages over the aerodynamic method in that (i) the large fetch requirement is not necessary, (ii) measurements of the air concentration and wind speed are needed at only one height, and (iii) the sensor is placed at a height that is relatively insensitive to the atmospheric stability so temperature and wind gradients and stability corrections are unnecessary. This approach is based on the trajectory simulation model described by Wilson et al. (1981a,b,c) and was recently used by Yates (1993) to simulate movement of pesticides away from the treated field. Wilson et al. (1983) and Majewski et al. (1990) have used the TPS method, among others, to determine the rate of pesticide and ammonia volatilization from field experiments. The pesticide flux is estimated from

$$f_z(0, t) = \frac{[\bar{u}(t) \bar{c}(t)]}{\Omega} \Big|_{z_{\text{inst}}} \quad [4]$$

where interval-average values of the wind speed, $\bar{u}(t)$, and air concentration, $\bar{c}(t)$, are obtained at the instrument height, Z_{inst} . The flux can be obtained by determining the ratio of the horizontal to vertical flux, Ω , using the trajectory simulation model. This ratio depends on the surface roughness and the upwind fetch distance (i.e., the radius of the circular plot) but does not depend on the wind speed. Although the method was originally developed for circular plots, it can be easily modified for square or rectangular plots, with a concomitant increase in computer calculations. Since, to our knowledge, this method has never been applied to rectangular fields, a brief description of the method and our modifications are included.

Trajectory Simulation

The TPS method is based on the trajectory simulation model. This model is used to simulate pesticide transport in the atmosphere using a particle-tracking algorithm and assuming that

the atmosphere experiences conditions of inhomogeneous turbulence. Wilson et al. (1981a,b,c) give a complete description of the method.

The simulation of a particle of air mass proceeds in an atmosphere in which the Eulerian velocity, $\sigma_w(z)$; time, $\tau(z)$; and length, $\Lambda(z) = \sigma_w(z)\tau(z)$, scales are assumed to vary only in the vertical direction. The velocity and time scales relate, respectively, to the effective or root-mean-square value of the vertical velocity and the persistence of the vertical velocity as a function of height. The horizontal wind speed varies only in the z direction and the time-averaged-value of the vertical wind speed is zero. It is assumed that the pesticide source is spatially uniform in the treated region (i.e., field); there is no source of pesticide outside the treated area; no degradation of pesticide occurs once it is in the atmosphere; and the surface roughness of the field, z_0 , is assumed to be constant. The simulation progresses using a transformed coordinate system that is related to the Lagrangian length scale. In this coordinate system, the turbulence is assumed to be homogeneous (i.e., constant length, velocity, and time scales).

The vertical dimension in the atmosphere is discretized into N layers, and the height of each layer is determined using $Z_i^* = (i - 0.5)\Delta Z^*$, where Z^* represents the transformed coordinates. The actual vertical height is related to the transformed height from

$$dz = \frac{\Lambda_L(z)}{\Lambda_L(H)} dz^* \quad [5]$$

where $\Lambda_L(z)$ is the Lagrangian length scale for the appropriate atmospheric stability conditions, the subscripted L indicates a Lagrangian frame of reference, and H is a reference height (m). Associated values for the horizontal displacement, Δx_i , are calculated using

$$\Delta x_i = u(z_i) \frac{\tau_L(z_i)}{\tau_L(H)} \Delta t_H \quad [6]$$

and at each time step, the vertical displacement height is given by

$$\Delta Z^* = \left(w_L(t_H) + \sigma_w(H) \tau_L(z_i) \frac{\partial \sigma_w}{\partial z} \right) \Delta t_H \quad [7]$$

where

$$w_L(t_H + \Delta t_H) = w_L(t_H) e^{-\frac{\Delta t_H}{\tau_H}} + \left(1 - e^{-\frac{2\Delta t_H}{\tau_H}} \right)^{1/2} \sigma_w(H) r \quad [8]$$

Equation 8 is a Markov chain and represents the random nature of the particle's movement in the Z^* coordinate system where r is a random variable with a standard-normal distribution.

The source area, which extends from $0 \leq x \leq X_{\text{max}}$, is discretized into M sections of equal length. A large number of particles is emitted from each section and tracked until the particles reach the collector located at X_{max} , which coincides with the position of the sampling mast in the field. From repeated applications of Eq. [6] through [8], the instantaneous vertical position of each particle is obtained and used to determine the current horizontal position increment for the current time step. Once a particle has reached the collector, the count of the appropriate level, Z_i^* , is incremented by one. As the number of particles released increases, the statistical character of the vertical distribution becomes fixed and the ratio of horizontal to vertical flux, Ω , as well as the instrument height, Z_{inst} , becomes known.

To obtain Ω , the simulation is conducted for strongly stable, strongly unstable and neutral atmospheric conditions. Plotting the results against height produces a curve similar to that shown in Fig. 1. The height where the three curves converge (operationally this is the intersection of the stable and unstable curves) is termed the *instrument height* and is the sensor location where the effects of atmospheric stability are minimized. The value of Ω is then used in Eq. [4] to provide an estimate of the surface flux. One difficulty using the TPS approach is the determination of the instrument height before initiating the experiment. This involves estimating the surface roughness, which may not be known until after the experiment begins (i.e., it cannot be estimated until after the plastic is placed on the field, which occurs at the time of application).

The curves shown in Fig. 1 depend on the distance between the sampling mast and the upwind edge of the treated area. For a circle with a central sampling mast, the distance X_{\max} is the same for all directions. For a rectangular area, however, the upwind source distance depends on the wind direction. To use the TPS method for these conditions requires that the simulation be conducted for several upwind source distances ranging from the smallest distance between the mast and the edge of the field to the largest distance and developing a relationship between wind direction and the instrument height or Ω . The procedure used here is to develop a relationship between the fetch distance and wind direction, which is accomplished using simple trigonometry. Next, a relationship between fetch and either Z_{inst} or Ω can be obtained through regression, using the information shown in Fig. 1, where the upwind fetch distance is the independent variable. Applying the trajectory simulation model for several fetch distances (i.e., 40, 70, 90, 105, 120, 135, 150, 170, and 190 m) provides the information necessary to identify the regression relationship between fetch and either Z_{inst} or Ω .

Integrated Horizontal Flux Method

The integrated horizontal flux method (Denmead et al., 1977; Wilson et al., 1982; Majewski et al., 1990) can be used to estimate the surface flux when the concentration, $c(z)$, and horizontal wind speeds, $u(z)$, in the atmosphere are known as a function of height. Assuming a spatially uniform source, the flux is estimated from a statement of mass balance, that is

$$f_z(0, t) = \frac{1}{L} \int_0^{\infty} \bar{u}(z) \bar{c}(z) dz \quad [9]$$

From this equation, the mass emitted from the surface upwind from a sampling point is equal to the mass that passes through a vertical plane of sufficient height to capture all the mass (i.e., of infinite extent) located at the sampling point. To use this method, the concentration profile at several heights must be determined, and the distance of the source area upwind from the sampling mast must be known. An advantage of this method over the aerodynamic method is that corrections for atmospheric stability are not needed since this approach is based on principals of mass balance.

RESULTS

Aerodynamic Method

Using the aerodynamic method (see Eq. [1]), measured values for the methyl bromide concentration and air temperature at 0.2 and 0.8 m above the soil surface together with measured wind speeds at 0.3 and 0.7 m, a value for the volatilization rate can be obtained. Shown

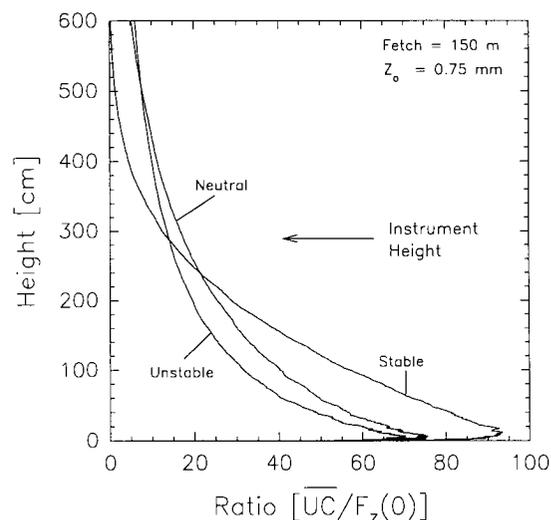


Fig. 1. Ratio of horizontal to vertical flux as a function of height from the trajectory simulation model (Wilson et al., 1981a,b,c) for neutral, unstable, and stable atmospheric conditions.

in Fig. 2A is the methyl bromide flux ($\mu\text{g}/\text{m}^2\text{s}$) that volatilized through the plastic covering the field as a function of time. The insert in Fig. 2A is an enlargement of the flux values beginning at the third day and continuing until the end of Day 7. The integer values (i.e., 1, 2, 3, 4, etc.) on the abscissa are indicative of midnight of the particular day. Therefore, the first sample was obtained during the afternoon of Day 0 and is displayed by the first small dot. The overall behavior of methyl bromide volatilization is a very high flux rate at the beginning of the experiment, caused by large methyl bromide concentrations under the plastic initially, followed by lower values for approximately 5 d after the application. On Day 5, the polyethylene plastic was removed (between $t = 5.6$ and 5.7 d), which caused a brief increase in the volatilization rate as the gas trapped under the plastic and in the near-surface soil was released. After Day 8, the volatilization rate was generally below measurable values. Similar data can be computed using the concentration data measured at 0.2 and 0.5 m or at 0.5 and 0.8 m. A summary of the total mass lost using this data is given in Table 1.

The highest volatilization rates generally occurred before midday during the 0800- to 1000-h sampling interval. This is caused by the environmental conditions that promote turbulent exchange, and can be illustrated by the Richardson's number. During this time interval, the thermal gradients in the atmosphere are increasing to approximately one-half of their daily maximum negative values. At the same time, the wind speed gradient is at the daily minimum; causing a large negative R_i . This indicates that buoyancy forces dominate, which in turn enhances the flux. Also, at this time the air temperature is rising, causing an increase in the diffusion through the polyethylene plastic (Kolbezen and Abu-El-Haj, 1977), allowing more methyl bromide to be released into the atmosphere. During the night, on the other hand, mechanical mixing is low along with nearly zero or slightly positive thermal gradients, indicating near-neutral or sta-

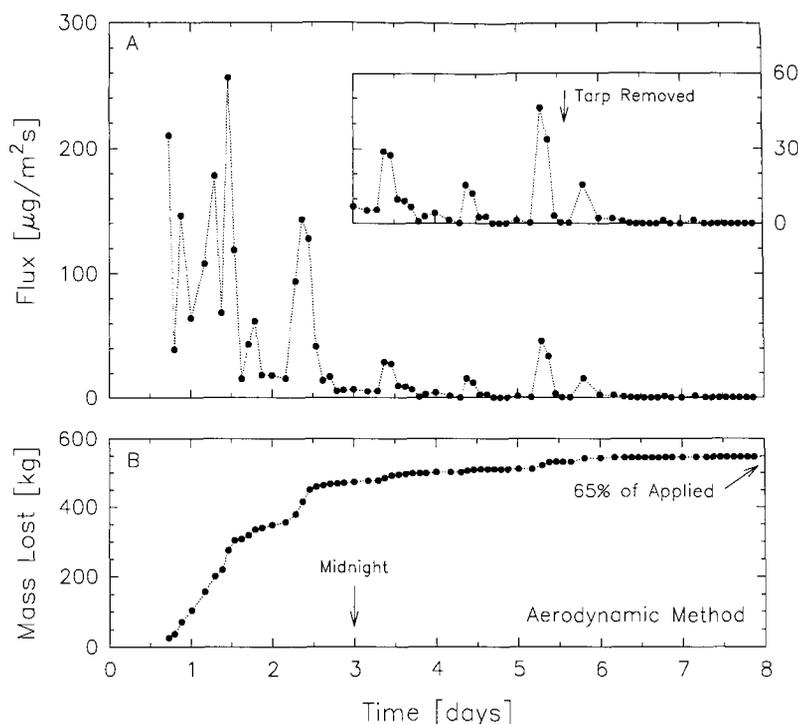


Fig. 2. (A) Methyl bromide flux ($\mu\text{g}/\text{m}^2\text{s}$) and (B) mass lost from volatilization as a function of time using the aerodynamic method. Insert is an expanded view of the flux.

ble atmospheric conditions. Coupled to cool temperatures, which decreases diffusion through the plastic, this causes reduced night time flux values. During the day, mechanical mixing is high along with buoyancy forces; producing moderately negative R_i . This indicates unstable conditions but the magnitude is much less compared with the 0800- to 1000-h interval.

Shown in Fig. 2B is the estimated mass (kg) lost from the field during the experiment as a function of time.

This was obtained by multiplying the flux measurement by the duration of the specific time interval and integrating over the area of the field (i.e., $34\,892\text{ m}^2$) and provides an estimate of the mass emitted from the soil surface for the experiment. The total methyl bromide loss is approximately 547 kg or approximately 65% of the applied mass (i.e., 843 kg). From the aerodynamic method data, it is clear that most of the methyl bromide mass that leaves the treated soil does so during the first

Table 1. Mass balance.

Flux method used	Mass lost while soil was covered	Percent lost while soil was covered	Mass lost after cover was removed	Percent lost after cover was removed	Estimated and applied mass difference†	Mass balance‡
	kg		kg		kg	%
Aerodynamic method (discrete)						$(62 \pm 11\%$ volatilized)
C:0.2 & 0.8 m‡	532	63.2	14	1.7	29	103.4
C:0.2 & 0.5 m	605	71.7	12	1.4	99	111.7
C:0.5 & 0.8 m	392	46.5	19	2.3	-107	87.3
Average (SD)	510 (88)	60.5	15 (3)	1.8	7	100.8
Aerodynamic method (profile)						$(67 \pm 6\%$ volatilized)
C:2-6; U:1-3	513	60.8	10	1.2	5	100.6
C:1-6; U:1-3	604	71.6	8	1.0	94	111.2
Average (SD)	558 (46)	66.2	9 (1)	1.1	50	105.9
Theoretical profile shape						$(60 \pm 3\%$ volatilized)
C:2-6; U:1-6	349	41.7	3	0.4	-166	80.3
C:3-6; U:1-6	569	67.8	3	0.3	54	106.3
C:4-6; U:1-6	557	67.2	9	1.1	48	105.7
Selective: C:2-6, C:3-6, C:4-6¶	528	63.6	8	0.9	18	102.1
Average (SD)	501 (26)	60.1	6 (2)	0.7	-12	98.6
Integrated horizontal flux						$(70 \pm 3\%$ volatilized)
Discrete C:1-6; U:1-6§	549	65.1	9	1.1	40	104.8
Profile C:1-6; U:1-6	596	70.8	9	1.1	88	110.4
Profile C:2-6, U:1-6	591	70.1	9	1.1	82	109.8
Average (SD)	579 (21)	68.7	9 (0)	1.1	70	108.3

† Mass applied: 843.1 kg; mass remaining: 0.261 kg; mass degraded: 324.9 kg.

‡ Method used to generate data in Fig. 2.

¶ Method used to generate data in Fig. 6.

§ Method used to generate data in Fig. 7.

48 h. In this case, about 308 kg ($\sim 36.5\%$) of the total applied methyl bromide is lost during the first 24 h and an additional 155 kg ($\sim 18.4\%$) was lost between 24 and 48 h. Of the 65% lost over the entire experiment, $<0.1\%$ is due to volatilization occurring after Day 6. This temporal behavior agrees with the work of other researchers studying methyl bromide emissions from fields (Yagi et al., 1993; Majewski et al., 1995) and is due primarily to the shallow injection depth and high air temperatures that occurred during this experiment.

Table 1 contains a mass balance summary for each of the flux estimation methods and data combinations that were used to determine the flux. Shown in the footnote to Table 1 are estimates of the mass applied, (843.1 kg), degraded (325 kg), and mass remaining in the soil (0.26 kg) from (Yates et al., 1996). A mass balance can be calculated by subtracting the mass lost from the field (i.e., volatilization and degradation) and the mass remaining from the amount applied. Negative mass differences, shown in Column 6, indicate less than complete mass recovery. The information in Table 1 was obtained using several data combinations for the methyl bromide concentration and several procedures for estimating the flux. Integrating over space and time yields a value for the mass lost. Several data combinations and analyses were used to provide supplementary information on the average behavior of the volatilization rate, to reduce the effect of errors or deviations in the data, and to identify aberrant behavior from any particular flux-estimation method.

For the aerodynamic method, five values of the mass volatilized were obtained. Three were estimated using the field-measured data in Eq. [1] and are denoted as

the aerodynamic method (discrete) in Table 1. Two estimates were obtained by fitting log-normal (with height) profiles to the measured concentration and wind speed data and are denoted as the aerodynamic method (profile) in Table 1.

For the aerodynamic discrete case, the time series of the measured concentration at 0.2 and 0.8 m (marked as C:0.2 and 0.8 m in Table 1), 0.2 and 0.5 m, and 0.5 and 0.8 m were used along with measurements of the air temperature at heights 0.2 and 0.8 m and the wind speed at 0.3 and 0.7 m above the soil surface. Incorporating these data in Eq. [1] produces a flux value for each sampling period. The most accurate value for the flux should be the one that uses the concentration data collected at 0.2 and 0.8 m above the soil surface, since the gradients for concentration, wind speed, and air temperature are all centered at 50 cm. The other flux values for the discrete case should be similar, however, since using the aerodynamic method requires a large fetch distance so that the gradients are fully developed. Under these conditions, nearly constant wind, temperature, and concentration gradients should exist near the surface in the fully developed layer. It is estimated from the aerodynamic discrete method that 525 kg (± 91 kg) or 62% ($\pm 11\%$) of the applied mass volatilized from the field. The mass balance ranged from 87 to 112% with an average mass balance of approximately 100.8%.

For the aerodynamic profile case, least squares regression equations were fitted to the concentration data collected at heights: 0.1, 0.2, 0.5, 0.8, 1.2, and 1.6 m above the soil surface as a function of log-height and the slope of the profile equation was used for the concentration gradient in Eq. [1] (i.e., $dC/d[\ln(z)]$). Two differ-

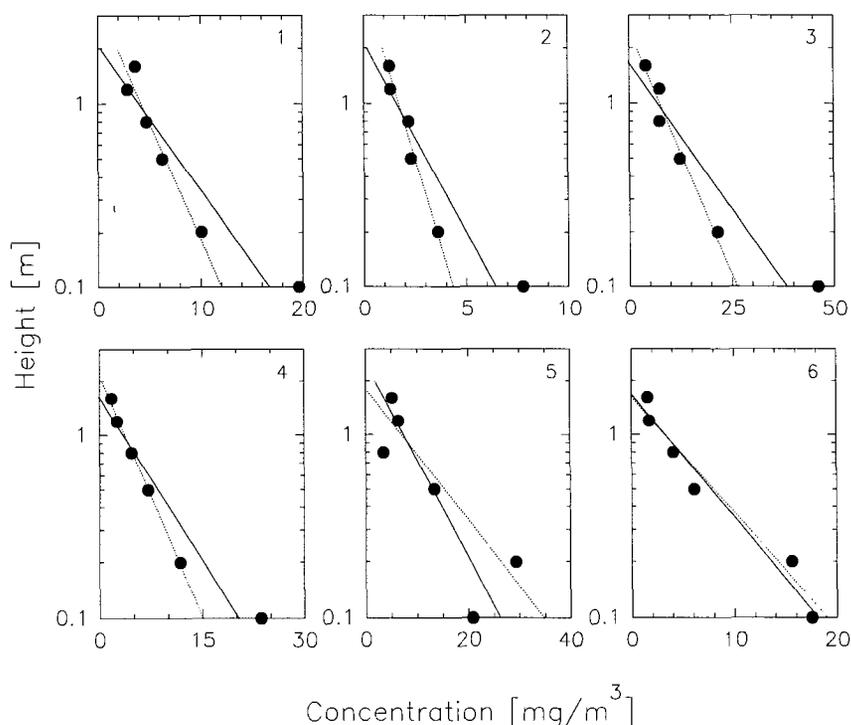


Fig. 3. Vertical profiles of methyl bromide concentration (mg/m^3) (dots) in the atmosphere for first six sample periods. Solid and dotted lines, respectively, are from linear regression with all measured data and the five measured values above 10 cm.

ent methods for describing the concentration profile are shown in Fig. 3 for the first six sampling intervals. The measured concentrations are shown as solid dots. The solid and dotted lines, respectively, indicate the use of linear regression with all six measured concentrations (denoted as C:1-6 in Table 1) or the five concentrations (denoted as C:2-6 in Table 1), which exclude the value at 10 cm. Generally, the measured concentration at 10 cm does not follow the logarithmic profile with height. This may be due to its closeness to the soil surface. According to Brutsaert (1982), log profiles generally occur in the dynamic sublayer, which begins at a height above approximately 1.5 to 3.5 h_o from the soil surface and extends some tens of meters, where h_o is a typical height of the roughness obstacles. Although the plastic material is relatively smooth, the surface of the field is not perfectly flat since soil is mounded at the point where two pieces of plastic are joined and surface irregularities can show through the plastic. No attempt was made to measure the obstacle heights, but a height of only $h_o = 4$ to 5 cm would be sufficient to place the concentration measurement at 10 cm slightly below the dynamic sublayer and therefore, may provide an explanation for why this value does not follow a logarithmic profile.

Shown in Fig. 4 are the wind speed profiles for the first six sampling intervals. Two logarithmic profiles have been fitted to the measured wind speed using linear regression. The solid line, denoted as U:1-6 in Table 1, uses all six measured wind speeds. The dotted line uses the three wind speeds at 0.1, 0.3, and 0.7 m and is denoted as U:1-3 in Table 1. Since the wind speed as a function of height is logarithmic only under neutral conditions (Rosenberg et al., 1983, p. 143), the regres-

sion relationship using the three lowest heights was used to more accurately fit the profile, and thus the wind speed gradient, in this region. These cases should produce identical values if the wind profile data were exactly logarithmic. The percent mass lost estimated from the aerodynamic profile case, using both the concentration and wind speed profiles, is approximately 62 to 73% of the applied methyl bromide. The mass balance for this approach ranges from 100.6 to 111.2%. The C:2-6, U:1-3 case is probably more representative of the actual mass lost since excluding the measured concentration at 0.1 m in the regression equation reduces the large deviations between the fitted and the measured concentration profiles.

Theoretical Profile Shape Method

A relationship that returns the upwind source distance given known values for the wind direction for this experiment is

$$\begin{aligned} \text{Fetch, } m &= 69/\cos(\theta); & 305.1 \leq \theta < 54.9^\circ \\ &= 98/\sin(\theta); & 54.9 \leq \theta < 138^\circ \\ &= -109/\cos(\theta); & 138 \leq \theta < 222^\circ \\ &= -98/\sin(\theta); & 222 \leq \theta < 305.1^\circ \quad [10] \end{aligned}$$

Using Eq. [10], a regression relationship was obtained, which gives the ratio of the horizontal to vertical flux, Ω , as a function of upwind fetch. Since the upwind distance also affects the instrument height, it was also necessary to obtain a regression relationship for Z_{inst} and interpolate between the available data to obtain the concentration at this height. These relationships are

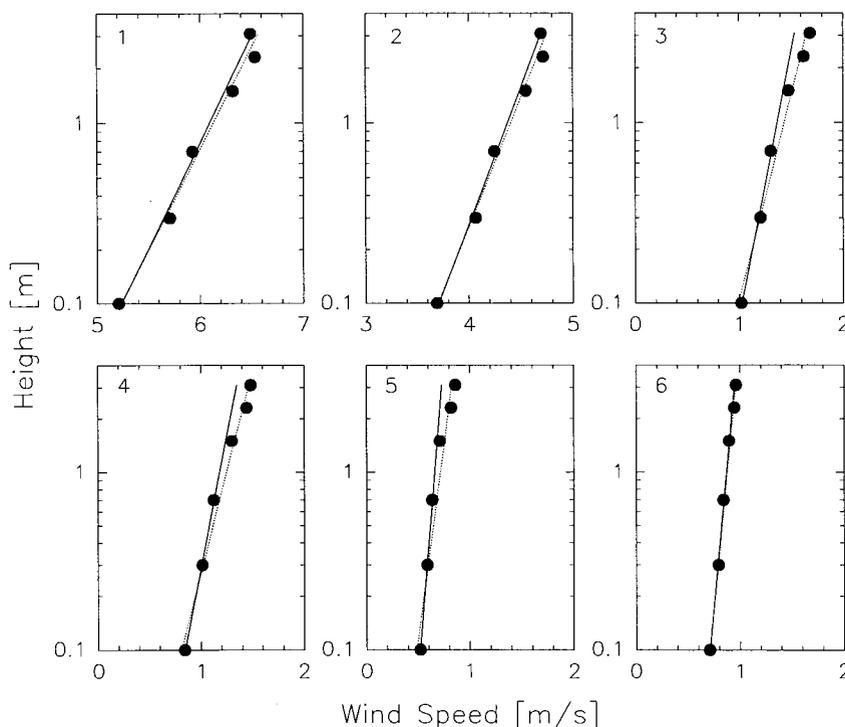


Fig. 4. Vertical profiles of wind speed (m/s) (dots) for first six sample periods. Solid and dotted lines, respectively, are from linear regression with respect to log-height using all wind speed data and the lowest three measurements.

shown in Fig. 5, where the circles indicate the Z_{inst} (A) and Ω (B) values for specified fetch distances and the lines were obtained using linear regression. With this information, the methyl bromide flux can be determined for any wind-direction averaging period. To obtain a flux value, first the measured wind direction and wind speed were averaged for the desired time interval. Using the averaged wind direction data and Eq. [10], the upwind fetch distance was determined. From fetch distance, Fig. 5A can be used to calculate the instrument height for the time interval. Since the sampling heights were fixed during the experiment but the instrument height varies with wind directions, the concentration and wind speed were estimated at the instrument height using regression relationships where a log-normal profile was fitted to the field-measured values. After estimating the wind speed and concentration, the ratio of the vertical to horizontal flux for a given fetch distance was obtained from Fig. 5B and the volatilization rate determined from Eq. [4].

Shown in Fig. 6A is a plot of methyl bromide volatilization ($\mu\text{g}/\text{m}^2\text{s}$) from the field during the experiment where each point represents either a 2- or 4-h averaging period. Like Fig. 2A, the insert in Fig. 6A is an enlargement of the flux values beginning at Day 3. The overall behavior is similar to the aerodynamic case, with the largest volatilization rates occurring during the first 24 h. The maximum flux value is off the scale used in Fig. 6 and is $786 \mu\text{g}/\text{m}^2\text{s}$. The zero-flux values are caused when the top (i.e., the height where the concentration is zero) of the log-profile for the concentration is below the estimated instrument height for the prevailing wind direction. This tends to occur during times when the flux would normally be low and probably indicates that the true concentration profile differs slightly from a log-

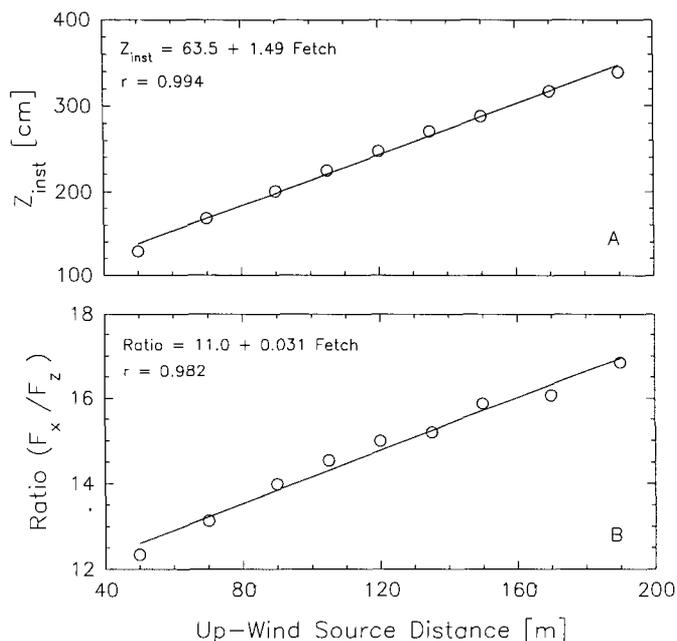


Fig. 5. Linear regression relationships between (A) upwind fetch distance and instrument height, Z_{inst} , and (B) ratio of the horizontal to vertical flux.

normal assumption. For these conditions the flux estimate is zero. The behavior of the flux is somewhat different than the aerodynamic case where the peak flux was preceded by two periods with lower values. Also, during the first 24 h, 401 kg or 47.5% of the applied methyl bromide was lost; during the next 24 h, an additional 92 kg or 10.9% was lost.

Shown in Fig. 6B is a graph of the mass lost (kg) estimated from the theoretical profile shape method. The estimates of the total methyl bromide emission range from approximately 352 kg (or 42%) to 571 kg (or 68%) and are listed in Table 1. The lower value of this range is probably not correct since this estimate is based on using the C:2-6 concentration profiles. When this information is used, many of the time intervals produce a zero flux. When the C:3-6 and C:4-6 profiles are used, additional nonzero flux values can be included in determining the total mass lost. The additional periods with a measurable flux increase the total emissions to the 65% range. The case denoted as *Selective* uses all 28 flux values obtained from the C:2-6 profiles along with 19 additional C:3-6 values (when C:2-6 produces zero flux) and three additional C:4-6 flux values. This is probably the most representative value since the greatest quantity of data is used in determining the flux. The mass balances ranged from nearly 80 to 106%, with an average mass balance of 98.6% ($\pm 3.4\%$).

Integrated Horizontal Flux Method

Two approaches were used to estimate the methyl bromide flux using the integrated horizontal flux method. The first involves a discrete approximation to the integral in Eq. [9], that is,

$$\int_0^{\infty} \bar{u}(z) \bar{c}(z) dz \approx \sum_i \bar{u}(z_i) \bar{c}(z_i) \Delta z_i \quad [11]$$

Alternatively, the flux was estimated by solving the integral directly. Given that the horizontal wind speed and methyl bromide concentration can be adequately characterized using linear equations with respect to the logarithm of height, that is

$$\bar{u}[z] = A + B \ln[z] \quad [12]$$

and

$$\bar{c}[z] = F + G \ln[z] \quad [13]$$

then substituting Eq. [12] and [13] into Eq. [9] and solving gives

$$\int_0^{\infty} \bar{u}[z] \bar{c}[z] dz = \int_{z_0}^{z_{\max}} \bar{u}[z] \bar{c}[z] dz = [(A - B)F + (2B - A)G + (BF + (A - 2B)G) \ln[z] + BG \ln[z]^2] z \Big|_{z_0}^{z_{\max}} \quad [14]$$

where z_{\max} is the estimated height where the concentration profile reaches zero and z_0 is the height, below which the wind speed is zero.

Shown in Fig. 7 are the methyl bromide flux (A) and mass (kg) lost from the field (B) estimated using all the

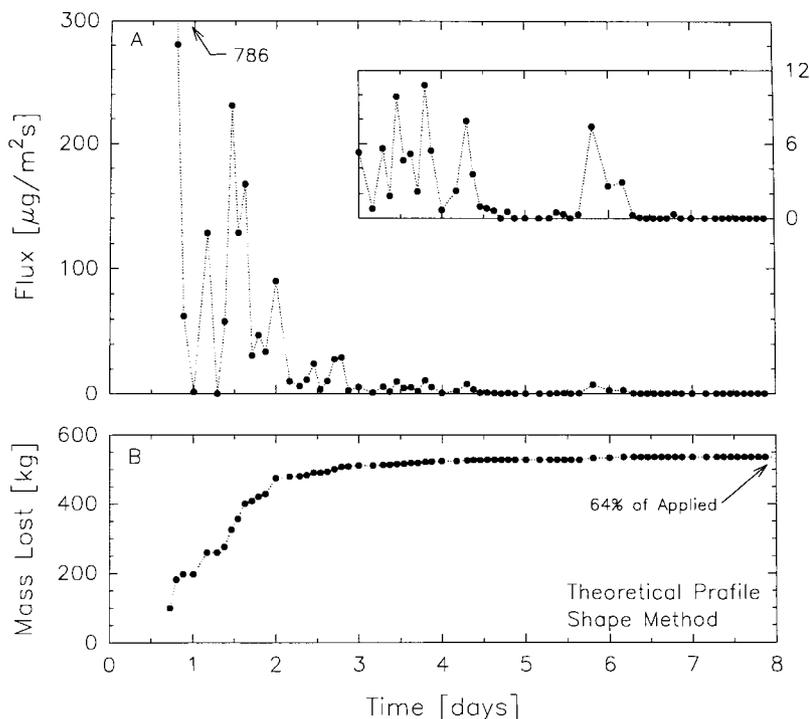


Fig. 6. (A) Methyl bromide flux ($\mu\text{g}/\text{m}^2\text{s}$) and (B) mass lost from volatilization as a function of time using the theoretical profile shape method. Insert is an expanded view of the flux.

measured concentration data in the discrete approximation to the integral. The dynamics of the methyl bromide emission rate at the start of the experiment are similar to the aerodynamic and theoretical profile shape methods with peak values early in the experiment and decreasing with time. During the first 3 d, the decreasing nature of in the flux with respect to time appears to be somewhat

smoother and has a more apparent exponentially decreasing shape. By 24 and 48 h after application, respectively, 402 kg (47.6%) and 103 kg (12.2%) of the applied methyl bromide was lost. The total fraction emitted to the atmosphere is estimated to be 66% with a 104.8% mass balance.

Fitting a linear regression equation to the logarithmic

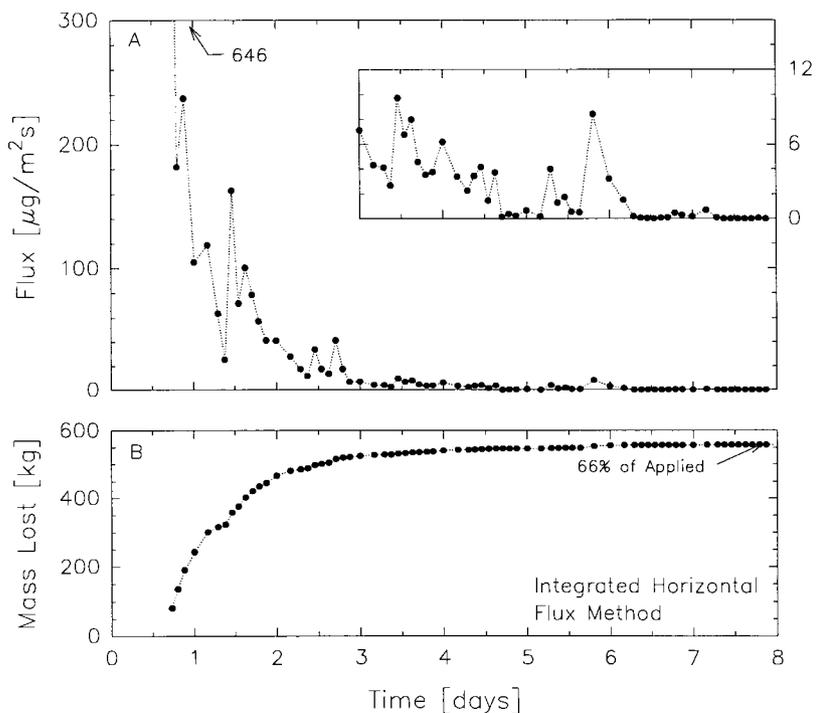


Fig. 7. (A) Methyl bromide flux ($\mu\text{g}/\text{m}^2\text{s}$) and (B) mass lost from volatilization as a function of time using the integrated horizontal flux method. Insert is an expanded view of the flux.

concentration-height data resulted in values for the mass lost ranging from 71 to 72%. The average mass lost using the integrated horizontal flux method is 588 kg (± 21 kg) or 69.8% ($\pm 2.5\%$). These values overestimate the mass lost from the production of Br⁻ method by approximately 15%.

CONCLUSIONS

An experiment was conducted to investigate the dynamics of methyl bromide volatilization from agricultural fields into the atmosphere. Methyl bromide was applied at a rate of approximately 240 kg/ha at a depth of 25 cm. The soil was immediately covered with a 0.025-mm (1-mil) polyethylene plastic, which was removed after 5 d. The atmospheric concentration and weather conditions were continuously monitored (24 h/d) until the air concentrations dropped below detectable values. Several values for the averaged total methyl bromide emissions from the field have been obtained and include an estimate from the methyl bromide mass degraded (61% of applied) along with estimates from the aerodynamic $64 \pm 9\%$ (of applied), theoretical profile shape $60 \pm 3\%$ (of applied), and integrated horizontal flux methods $70 \pm 3\%$ (of applied). The average percent mass recovery using all the flux methods listed in Table 1 is 867 kg, which is 102.8%. The total mass lost from this experiment is approximately 75% higher than the value reported by Majewski et al. (1995), who estimated the total loss to be approximately 36%. The differences in emission rate are probably due to the climatic conditions in the Monterey region compared with Moreno Valley. Decreased temperatures would cause a reduction in the diffusion through polyethylene plastic material (Kolbezen and Abu-El-Haj, 1977) and increasing the residence time in the soil causing a greater amount of methyl bromide to be degraded in the soil. The range for total emissions described herein also differs from the results of Yagi et al. (1993) and Yagi et al. (1995), who report values of approximately 87 and 34%, respectively, for experiments with a similar methyl bromide application methodology. It is highly advisable that a mass balance be conducted along with the use of several methods for estimating the flux so that the accuracy of the total emissions rate from agricultural fields can be determined. This will help to identify errors when determining the flux, the field-scale degradation or the methyl bromide remaining in the field.

The large levels of emissions that result when methyl bromide is applied at a shallow depth and the soil covered with a relatively permeable polyethylene tarp suggest that this application method is not efficient in terms of methyl bromide use for pest control nor in protecting the atmosphere from anthropogenic sources of methyl bromide. Research is urgently needed to develop suitable methods for containing methyl bromide in soils at lower rates of usage and for longer periods of time so that soil degradation can occur. If improved application practices can be found and not produce any economic impediments, then a significant lowering of the anthropogenic methyl bromide emissions would occur without any loss in pest-control efficiency.

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ERRATUM

The Cadmium Content of British Wheat Grain

A.M. Chaudri, F.J. Zhao, S.P. McGrath, and A.R. Crosland; J. Environ. Qual. 24:850-855 (1995).

The German limit for Cd in wheat grain of 0.1 mg kg⁻¹ fresh wt. (0.12 mg kg⁻¹ dry wt.) (BGA, 1986) has been mistakenly labeled as the *WHO limit* in the above paper. There is as yet no FAO/WHO Cd in wheat grain limit.

Reference

BGA (Bundesgesundheitsamt). 1986. Richtwerte '86 für Blei, Cadmium und Quecksilber in und auf Lebensmitteln. *Bundesgesundheitsblatt* 29:22-23.