

Fumigants

Environmental Fate, Exposure, and Analysis

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Chapter 11

Emissions of Methyl Bromide from Agricultural Fields: Rate Estimates and Methods of Reduction

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Methyl bromide, a soil fumigant, is under intense scrutiny due to evidence which suggests that it damages the stratospheric ozone layer. Because of this, methyl bromide is scheduled for phase-out by 2001. The National Agricultural Pesticide Impact Assessment Program has determined that there will be substantial adverse economic impacts on the agricultural community if the use of methyl bromide is restricted. This has prompted numerous scientists to: study the environmental fate and transport of methyl bromide; search for replacement chemicals and/or nonchemical alternatives; and develop new methodology which improves containment of methyl bromide (or any alternative fumigant) to the treatment zone, while maintaining adequate pest control. This paper reports on several recent experiments to measure of methyl bromide emissions from agricultural operations. Information is also provided on the processes and mechanisms which must be fully understood if reliable methods for reducing atmospheric emissions are to be obtained, without a reduction in pest control.

For decades, methyl bromide (bromomethane, MeBr) has been used for the control of nematodes, weeds and fungi. Recently, it has come under scrutiny as a chemical which depletes stratospheric ozone. Under the provisions of the U.S. Clean Air Act, which calls for the discontinuation of compounds which deplete ozone, MeBr is scheduled for phase-out by the year 2001. The USDA National Agricultural Pesticide Impact Assessment Program (I) conducted an assessment of the economic impact of eliminating MeBr use and determined that there will be a substantial adverse impact on the agricultural community. These effects will be most strongly felt in two states, California and Florida, which are the primary users of MeBr. It has estimated (I) that a MeBr phase-out in soil fumigation will cause \$1.5 billion dollars in annual lost production in the United States. This estimate is conservative, however, since it

ignores post-harvest, non-quarantine uses and quarantine treatments of imports and other future economic aspects such as lost jobs, markets, etc. In terms of specific commodities, major crop losses would occur with tomatoes (\$350 M), ornamentals (\$170M), tobacco (\$130M), peppers (\$130M), strawberries (\$110M) and forest seedlings (\$35M).

Over the past decade, concern has increased that halogenated gases emitted into the atmosphere are destroying the stratospheric ozone layer. The Ozone Assessment Synthesis Panel of the United Nations Environmental Programme (UNEP) states that the hole in the Antarctic ozone layer is due primarily to increases in chlorine- and bromine-containing chemicals in the atmosphere. Although 90 to 95% of the ozone loss is thought to be from chlorinated compounds (2), attention has been focused more recently on MeBr because bromine is believed to be 40 times more efficient than chlorine in breaking down ozone on a per atom basis (3). Although the largest effects from ozone-depleting gases have been observed in the southern hemisphere, there are indications that atmospheric ozone is also decreasing in the northern hemisphere.

To complicate matters, there is a great deal of uncertainty in the estimates of global sources of bromine. For example, it has been estimated that natural bromide-gas production by marine plankton in the oceans contributes 50-80% of the global burden. Agricultural fumigation, however, represents approximately 15-35% (4-7) and recent figures indicate that biomass burning may contribute up to 30% (8). The oceans may act as a net sink, rather than a source (9) of bromine-gases; and the deposition onto soil and subsequent microbial degradation may be another important pathway for removing MeBr from the atmosphere (10). Also, although agricultural emissions represent a significant fraction (i.e., 15 to 35%), even if MeBr is no longer used in agriculture, large amounts of bromine-gases will continue to exist in the atmosphere and, therefore, must be considered a natural condition. Even so, it is desirable to develop improved methods for reducing agricultural MeBr (and alternatives) emissions to the atmosphere so that anthropogenic contributions are minimized.

In this paper, recent measurements of MeBr emissions under field conditions are summarized, and a field study in which three independent methods were used to obtain the emissions rate is described. Based on recent field and laboratory studies and published information, approaches for reducing MeBr emissions are also discussed.

Measured Emissions Rates

There have been several recent experiments conducted to obtain information on MeBr emissions from typical agricultural operations. These studies used various methods for estimating the emission rate and include: an increase in soil Br⁻ concentration as a result of MeBr degradation (11), atmospheric flux method (12,13) and enclosed flux chamber method (14-16). Each method has advantages and disadvantages which can make the interpretation of the experimental results somewhat difficult. The Br⁻-appearance method assumes that the difference between the MeBr mass applied and mass degraded (i.e., Br⁻ produced) was released into the atmosphere. Therefore, measuring Br⁻ in the soil provides a method for estimating the total atmospheric emission. An advantage of this method is the ease of analyzing the

Br^- content of soils. A disadvantage is the large number of soil samples necessary to obtain an accurate field-scale estimate of degradation at all depths (11). Also, no information about the dynamics of MeBr emissions can be obtained using this method. Atmospheric flux methods are fairly complex, require numerous measurements of MeBr concentration and other meteorological parameters and may require assumptions concerning the behavior of the atmosphere. Advantages are that the methods are well tested, they provide a field-scale average total emission rate and they provide information on the dynamics of the volatilization process. The flux chamber method (17-19) is one of the simplest methods for measuring pesticide flux, but it suffers from several disadvantages. The method measures the flux over a small area which can cause the estimated flux rate to be highly variable, the flux estimates are sensitive to the placement of the chambers relative to the position of MeBr injection (i.e., distance to the source), and the presence of chamber can affect the area sampled (especially the local temperature and relative humidity). These can have a tremendous effect on experimental uncertainty.

Yagi et al. (14) conducted an experiment to measure the MeBr emission from a southern California field using passive flux chambers. MeBr was applied at approximately 25 cm depth and the soil surface was covered with polyethylene plastic. The authors estimated that 87% of the total MeBr applied to the field escaped into the atmosphere. This is the highest reported estimate for MeBr emissions when the compound was injected at shallow depth and the field was covered with plastic. The high emission rate may have been due, in part, to the high bulk density of the soil and the presence of a wetter soil layer at 60 cm depth. The authors indicated that this value was higher than expected given other estimates based on mathematical models (20,15), but was similar in magnitude to the losses observed in glass-house studies (21). To verify these results the authors returned to the field to collect Br^- information to provide a rudimentary mass balance estimate (15). In addition, these investigators conducted a second experiment using the same procedures as their first experiment and found that only 34% of the applied MeBr escaped to the atmosphere. This value is 61% lower than the result of their first experiment. This sort of variability is not unexpected for several reasons: 1) only 10-15 samples of the volatilization rate were obtained during each 7-day experiment, generally at the high point during the day; 2) only a few soil samples were taken to measure Br^- concentrations and soil Br^- concentration has been shown to be highly variable (11,22); 3) the soil Br^- concentration after fumigation was measured to only 90 cm; and 4) for the first experiment, initial Br^- concentration was available only at depth of 3.0 cm and was extrapolated downward. An additional source of variability may be the internal chamber temperature. Yates et al. (16) demonstrated that chambers can produce erroneously high volatilization rates if their presence on the tarp causes an increased internal chamber temperature relative to the outside environment. Yagi et al. (14,15) did not correct their volatilization rates for this effect.

In a study conducted in a strawberry field, Majewski et al. (12) found that 32% of the applied MeBr was emitted into the atmosphere during the first 6 days following application. This value is approximately the same as that from the second study of Yagi et al. (15). The MeBr application rate for this experiment was 392 kg/ha and the

flux density was measured using the aerodynamic method (23). The reported total loss fell into the 30-60% range noted in the Montreal protocol (20), but a mass balance was not conducted. More information on this experiment is given in this proceedings.

An Experiment with Three Independent Measures of Total Emissions

An experiment (11,13,16) was conducted at the University of California's Moreno Valley Field Station on a 4-ha field between August 26, 1993 and September 13, 1993. The soil in this field is a Greenfield sandy loam. MeBr (applied as 99.5% MeBr (CH_3Br) and 0.5% chloropicrin (CCl_3NO_2)) was applied at a shallow depth of 25 cm, at a rate of 240 kg/ha, and the field was covered with 1 mil polyethylene plastic. Three independent methods were used to give estimates of the MeBr emission rate and total loss.

Estimating Total Loss from Br^- Appearance. To estimate the total MeBr mass converted to Br^- , numerous soil cores were taken to a maximum depth of 7 m. Four soil cores were taken in the center of the field to a depth of 2 m and one to 3 m prior to applying MeBr to provide background concentrations. The Br^- concentrations were measured using an ion selective electrode connected to an Accumet 25 pH meter (Fisher Scientific Co.) at 0.3-m depth increments. After the experiment, 25 cores to a depth of 5 m and 5 cores to 7 m were taken randomly in the field. These cores were sectioned at 0.1 -m intervals from the surface to a depth of 1.0 m and at 0.2-m intervals from 1 to 7 m. Comparing the pre- and post-treatment Br^- concentrations, it was determined that additional background concentrations were needed to reduce spatial variability and improve the accuracy of the estimate of the background Br^- concentration. Therefore, 30 additional soil cores to 7 m were obtained in the field adjacent to the experimental site which had the same soil type, cropping and irrigation history but was never fumigated.

Figure 1 shows the background Br^- [mg/kg] concentration on a dry soil weight basis taken prior to application (open squares). The samples taken from the adjacent field are shown as closed diamonds. Also shown on these curves is a bar which indicates an average standard deviation for the curve calculated by averaging the standard deviations at each depth and, therefore, is the same at every point. The Br^- concentration 36 days after application is shown as open circles. An estimate of the total MeBr lost to the atmosphere can be obtained from the difference between the initial and final curves and converting from Br^- mass to MeBr mass.

Using the information in Figure 1, $325(\pm 164)$ kg or 39% ($\pm 19\%$) of the applied MeBr was degraded to Br^- . Since the MeBr mass remaining in the field was estimated to be less than 0.05% at the time of sampling, the total loss from volatilization is estimated to be approximately 518 (± 164) kg. The spatial and measurement variability introduces uncertainty into the Br^- mass calculation as shown by the standard error of ± 164 kg. Uncertainty in the measured Br^- directly affects the certainty in the estimate of MeBr volatilized from the field, producing $61\% \pm 19\%$.

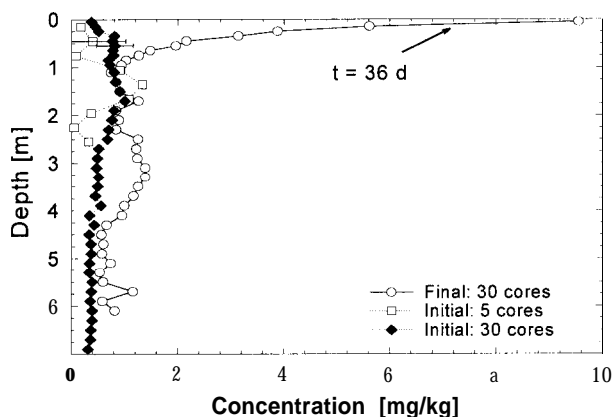


Figure 1. Bromide ion concentration as a function of depth in the field.

Field scale variability must be considered when obtaining the average Br^- concentration in the field. This is especially important when this information is used in estimating the total MeBr lost from the field. This can be illustrated as follows. If the estimate of the mass is obtained using the 5 background soil cores to a depth of 2 and 3 m (i.e., 45 samples), the total loss is estimated to be 298 kg or 35.3%. If in addition, the samples for depths below 3 m taken from the 30 cores located in the adjacent field are used to extend the initial distribution below 3 m (i.e., 500 samples), the total loss is estimated to be 435 kg or 48.4%. When only the 30 soil cores are used and all depths considered (i.e., 1100 samples), the mass loss is estimated to be 518 kg or 61%. This demonstrates that numerous deep soil cores are needed to adequately estimate MeBr degradation in soil and that the 5 soil cores from the field interior happen not to produce an accurate field-scale average of the initial Br^- concentration. The estimate of the field-average Br^- mass which makes use of the most samples has the highest probability of being the most accurate.

Estimating Emissions from Atmospheric Flux Methods. To collect air samples above the fumigated field which could be analyzed for MeBr, a sampling mast was constructed (24) and placed in the center of the field. The mast held coconut-based charcoal sampling tubes at heights of 0.1, 0.2, 0.5, 0.8, 1.2, and 1.6 m above the field surface. A vacuum system was used to draw air (at 100 mL/min) through the sampling tubes to extract the MeBr gas. The duration of the sampling intervals was either 2 or 4 hours. The atmospheric concentration and weather conditions were continuously monitored 24 hours a day until the air concentrations dropped below detectable limits. The method used to analyze the charcoal sample tubes and the details of the error analysis resulting from sample handling are given by Gan et al. (25,26).

The aerodynamic (23), theoretical profile shape (27,28) and integrated horizontal flux (29) methods were used to estimate the total MeBr emission. Since these flux-estimation techniques use the same gas concentration data, they do not

represent completely independent flux estimates. However, if the three methods produce similar emission rates, this would be supportive evidence of valid experimental procedures.

Figure 2a shows the flux density during the first 7 days of the experiment and Figure 2b reports the cumulative mass lost. The solid line was obtained from the aerodynamic method.

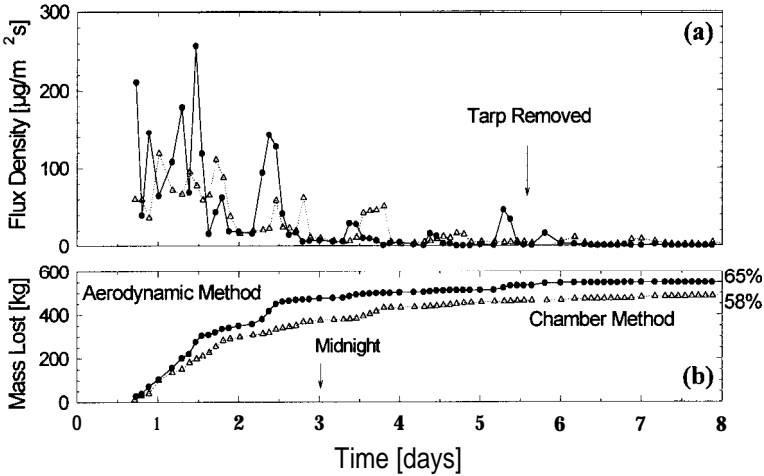


Figure 2. MeBr flux density (a) and mass lost (b) from the field during the first seven days of the experiment.

The highest flux density occurred at the beginning of the experiment when nearly 36% of the applied MeBr mass was lost during the first 24 hours after application. The highest flux rates occurred during the late morning and early afternoon when temperatures were highest and the atmosphere was unstable. Cooler temperatures, light winds and neutral to stable atmospheric conditions were present at night; generally reducing the flux. Using the aerodynamic method, the total emission was estimated to be 62% ($\pm 1\%$) to 67% ($\pm 6\%$) of the mass applied to the field. For the theoretical profile shape and integrated horizontal flux methods, respectively, the estimates were 61% $\pm 3\%$ (of applied) and 70% $\pm 3\%$ (of applied). A mass balance was calculated for each method used to estimate the flux (Table 1). The average mass recovery using all the flux methods was 867 kg (± 83 kg), which was 103% ($\pm 10\%$) of the applied mass (i.e., 843 kg). The range in the mass balance percent (i.e., percent of applied mass that is measured) was from 97% to 108%. The averaged mass balance percent for the discrete aerodynamic method, which involved using the measured data directly, was approximately 101%.

Table 1. Total Amount of MeBr Volatilized During the Experiment and Mass Balance

Flux Method Used	Mass Lost [kg]	Percent Lost [%]	Mass Balance [†] [%]
[‡] Aerodynamic, (discrete)	525 (± 91) [']	62.2	101
[‡] Aerodynamic, (profile)	568 (± 47)	67.3	106
['] Theoretical Profile Shape	506 (± 29)	60.1	99
[‡] Integrated Horizontal Flux	588 (± 21)	69.8	108
['] Flux Chamber, (corrected)	464 (± 170)	58.8	97

^t Mass Applied 843 kg; Mass Remaining 0.26 kg; Mass Degraded 325 kg

[‡] Data from (13)

['] Data from (16)

[§] Values in parentheses are standard deviations

The fraction of the applied mass lost from this experiment is approximately double the value reported by Majewski et al. (12) who estimated the total loss to be approximately 32%. This is probably due to differences in the climatic and soil conditions between the Monterey region and Moreno Valley. Lower temperatures in Monterey would cause a reduction in the diffusion through polyethylene plastic material (30) and increase the residence time in the soil. This would facilitate greater MeBr degradation in the soil and reduce the total loss to the atmosphere. The range for total emissions described herein also differs from the results of Yagi et al. (14,15) who reported values of approximately 87% and 34%, respectively, for experiments with a similar MeBr application methodology.

Estimating Emissions using Flux Chambers. An independent estimate of flux was obtained using three flow-through chambers (31,18). The MeBr volatilization rate and cumulative mass lost from the field was obtained by integrating the chamber flux density data shown in Figure 2 (dashed line) over the entire field and course of the experiment. During the first 24 hours after application, approximately 365 kg or 45% of the applied mass volatilized from the field. During the next 24 hours, an additional 202 kg or 25% was lost to the atmosphere.

The total mass emitted from the field was estimated to be 811 kg, which is about 96% of the 843 kg that was applied to the field. The mass balance calculated using this data was 135%, which was not consistent with the estimates derived from

the soil Br^- data and atmospheric flux methods. This discrepancy prompted an investigation of the flux chamber data.

The air temperature inside the chambers used in the experiment was found to be much higher than the air temperature outside and was highly correlated with the diurnal variation in incoming solar radiation. Figure 3 shows the MeBr flux density through polyethylene film in response to changes in the ambient temperature. The plastic used during this experiment is shown as open boxes (other data from (30)). Using this information, a method was developed to correct the chamber flux density data for enhanced flux caused by increases in the temperature inside the chamber (16).

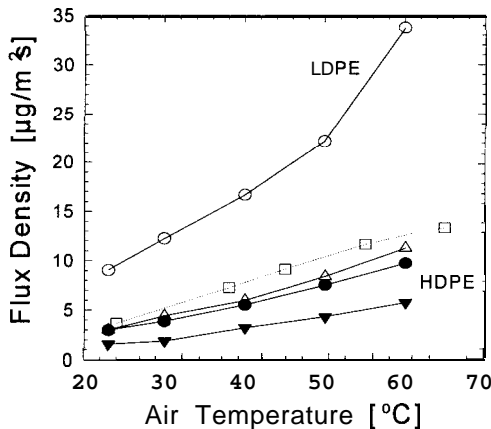


Figure 3. Temperature dependence of the flux density through polyethylene. Higher flux density is equivalent to higher emissions.

After correcting for temperature, the total mass emitted from the field was estimated to be about 496 (± 175) kg as opposed to 811 (± 303) kg. The loss represents about 59% of the total applied mass, which more closely follows the results from the other estimates. During the first 24 hours after application, approximately 227 kg (27% of applied) of MeBr was lost, which is 46% of the total emissions. During the next 24 hours, an additional 117 kg (14% of applied) was lost. The corrected total mass lost is about 3 to 10% lower than the estimates from the other methods. A mass balance of 97% was obtained for the corrected measurements (Table 1).

Factors Important in Reducing Emissions

There are many soil-chemical processes which affect the fate and transport of fumigants, including MeBr. Generally, three factors must be controlled to reduce emissions while maintaining adequate efficacy: containment, degradation and soil-gas concentration (i.e., effective dosage). Unless each of these factors is controlled, unacceptable emissions will likely result. For example, in the absence of degradation,

perfect containment alone will not produce lower emissions unless the field remains covered indefinitely. A balance must be achieved with adequate containment together with sufficient degradation to reduce the amount of MeBr in the soil prior to removing the plastic cover, all of this, while maintaining adequate soil concentration levels to control pests.

Laboratory Experiments. Soil columns were used to determine how injection depth, use of plastic covers, soil water content, bulk density and soil organic matter affects the total MeBr loss from soils. The columns were 60 cm in length and have a closed bottom which restricts downward diffusion of MeBr. This restriction causes the volatilization rates to be overestimated when compared to an infinite-length column which is analogous to the field. A diffusion model was used to correct the emission rates so that they relate more closely to field situations. The corrected results are used in the discussion below. In brief, four steps were involved. 1) Experiments were conducted to obtain the emission rate and the soil-gas concentration at different times for the selected management factors. 2) Multiple sets of the measured MeBr concentrations in soil air were used in a gas-diffusion transport model to obtain the model parameters under the experimental conditions (e.g., when an impermeable barrier occurs at 60 cm). 3) These parameters were used in a similar model to estimate MeBr volatilization rates for columns without a barrier, which is analogous to the field. 4) The results from the two models were used to obtain the ratio: (simulated total loss without barrier)/(simulated total loss with barrier) and the measured laboratory values were multiplied by this ratio to give an estimate of the volatilization rate in a field soil experiencing similar conditions.

Containment. Containment is necessary to hold the gas at the treatment location and provide sufficient time for pest control. Without adequate containment, significant fractions of applied MeBr will be lost to the atmosphere. The need for containment is due to MeBr's high mobility as a result of its high vapor pressure (approximately 1420 mmHg at 20°C) and low boiling point (3.56 C). Because of these properties, a large fraction of MeBr exists in the vapor phase at temperatures and pressures that normally occur in the field. Since the gas-phase diffusion coefficient is nearly 10,000 times greater than in the liquid phase (32), pesticides which have a large vapor pressure easily move through soil (33-35). Factors that affect containment include: use of plastic, the properties of plastic, injection depth, soil bulk density, soil water content, soil cracking, and other mechanisms which promote or retard movement. For example, shortly after injection, pressure-driven flow may dominate MeBr movement in response to phase-change expansion and the initially high gradients near the injection point. This can cause MeBr to quickly move to the soil surface where it can escape into the atmosphere. Other processes may also be important in moving fumigants through the root zone. For example, changes in barometric pressure (36), pressure effects caused from wind at the surface and density sinking (33) all may induce a mass flow. While it may be possible to take advantage of many soil factors to aid in containing MeBr, the inherent spatial variability of soils make it difficult to ensure emissions control for every situation.

Plastic Films. Probably the most common and the most predictable method to improve containment and reduce the amount of MeBr leaving the treated soil is the use of plastic films. Covering the field with plastic can reduce the amount of MeBr volatilized by inhibiting transport from the soil into the atmosphere. Advantages of using films are that the properties and condition of the film is known in advance and films are more uniform in space and time compared to soil. Therefore, there may be a higher certainty of effective containment when films are used compared to soil-water based methods. Also, the level of containment can be controlled by altering the plastic material used. For example, new plastics are available which are highly impermeable to MeBr diffusion (Table 2).

Table 2. Flux Density [$\text{mg}/\text{m}^2/\text{h}$]^a of fumigants through 1.4-mil high-density polyethylene film and 1 -mil Hytibar[®] Film^b

Fumigant	Flux Density ^c Through 1.4-mil Polyethylene [$\text{mg}/\text{m}^2/\text{h}$]	Flux Density Through 1 -mil Hytibar ^b [$\text{mg}/\text{m}^2/\text{h}$]	Material	Methyl Bromide Flux Density [$\text{mg}/\text{m}^2/\text{h}$]
Methyl Bromide	7.4	0.1	2-mil silver mylar	1.4
Methyl Iodide	8.9	0.06	2-mil mylar	2.2
(E) 1,3-D	87	0.2	5-mil mylar	2.1
(Z) 1,3-D	62	0.2	1 -mil polyethylene	16.3
MITC	100	0.5	6-mil polyethylene	5.3
Chloropicrin	17	not measured	Saran aluminum foil	3 0.2

^a The flux density is: mg diffusing through 1 m^2 of film in 1 h while maintaining a 1 mg/L concentration gradient across the film.

^b Hytibar[®] film is a high-barrier film manufactured in Belgium.

Traditional 1 mil (i.e., 0.025 mm) high-density polyethylene is relatively permeable to MeBr (30,37) and the permeability is affected by the ambient temperature. Using this material in warm temperatures can result in significant losses (i.e., 30 to 60%).

However, under cool conditions and with a relatively deep injection depth, this plastic may provide adequate containment. Since experiments have shown that nearly all of the applied MeBr may leave the treated soil zone after a few days when injected at a shallow depth into bare soil (12), under most circumstances it is better to use plastic than to leave the soil surface uncovered.

Table 3 provides a summary of the total MeBr emission in percent of applied MeBr for both tarped and untarped treatments following injection into soil columns (38). After correcting the flux for the presence of the lower boundary, the total emission loss of MeBr was 82% under bare surface conditions, and 43% under tarped surface conditions when injected at a 20-cm depth. For a 30-cm injection, 71% of the applied MeBr was emitted for the untarped column and 37% from the tarped column. When injected at 60-cm, the total emission loss was 38% under bare surface conditions, and 26% under tarped conditions.

Table 3. Effects of Injection Depth and Use of Plastic Films

Injection Depth	Total Emissions (Measured) (%)	Total Degradation (%)	Mass Balance (%)	Total Emissions Corrected Using Diffusion Model (%)
Tarped Columns				
20 cm	59	36	94	43
30 cm	52	39	91	37
60 cm	45	46	91	26
Non-Tarped Columns				
20 cm	91	12	102	82
30 cm	83	1.5	98	71
60 cm	60	36	96	38

When the soil surface was not covered with the polyethylene sheet, MeBr volatilization was extremely rapid, with as much as 80-90% of the total loss occurring during the first 24 h. In contrast, when a tarp was present on the soil surface, the maximum volatilization flux was significantly smaller, with only 30 - 45% of the overall loss occurring during the first 24 h. While measurable volatilization rates continued for a longer time (7-10 days) compared to the untarped columns (3-4 days), total emissions were significantly lower in tarped columns.

Similar results were observed in two parallel field experiments (12). In an untarped field, MeBr emission after 25-30 cm injection was measured to be 89% over the first 5 days after application; while in a tarped field located 6 km away, the emission rate was 32% over the first 9 days after application. Based on the results from this study and the few recently reported field studies, it is clear that MeBr emission rate in a tarped field is considerably lower than under untarped conditions when injected at shallow depth (20-30 cm). Films with lower permeability, such as Saranex[®], should produce even greater reductions. Also, since MeBr is retained in the soil much longer under films with lower permeability, it should be possible to reduce the application rate

without sacrificing the fumigation efficacy (39). Reducing the application rate when high barrier films are used may provide a means for producing significant decreases in emissions from the combination of lower application rates and lower emissions.

Injection Depth. The depth of application is also an important factor affecting the amount of methyl bromide escaping into the atmosphere. In laboratory soil columns, when the application depth was increased from 20 to 60 cm, the MeBr emission rates decreased by 54% under untarped conditions, and 40% under tarped conditions (Table 3). The emission rate for the tarped, 60-cm application was the lowest estimated loss observed from any of the treatments (Table 3). This supports the results from a recent field experiment conducted at the Moreno Valley Field Station (Yates et al., 1994, unpublished data) where the MeBr emission rate for a bare soil, deep injection application was determined. MeBr was injected at approximately 68 cm at a rate of 322 kg/ha (291 lb/ac), a total mass of 1134 kg for the entire fumigated field. The average, maximum and minimum air temperatures during the first 7 days of this experiment were 15.1, 30.2, 4.5 °C, respectively. Shown in Figure 4 is the Br⁻ concentration reported as mass per sample length before and 3 and 9 months after application. From these data, it was estimated that 879 kg or (78%) of the applied mass was degraded to Br⁻; or approximately 2 1% of the applied mass was lost to the atmosphere. This is 66% less than the 62% total loss reported by Yates et al. (11, 13,16) from an adjacent field and can be attributed to the deeper injection depth and a warmer average air temperature during the earlier experiment (24.2, 34.2 and 13.6 °C, for the 7 day average, maximum and minimum temperature).

These results are also in agreement with recent predictions (35) using a transport model. Under hypothetical conditions, it was estimated that increasing the

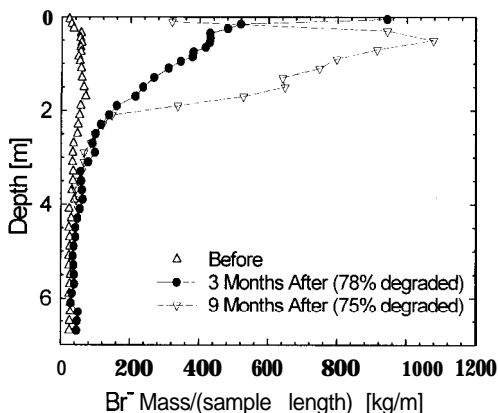


Figure 4. Bromide ion concentration as a function of depth in the field

injection depth from 25 to 45 cm would decrease the MeBr emission rates from 45 to 28% when the soil was tarped. From these findings, it can be concluded that placing

MeBr at a greater depth is another effective approach for minimizing its emission into the air during soil fumigation.

Soil Water Content. Increasing soil water content has been considered as a means for controlling MeBr movement (33,35,37). The effect of water content on MeBr volatilization can be explained by the interactions of soil water content and the retardation factor, $R_d = (\theta + k_d \rho_b) / k_h + \epsilon$, and tortuosity factor, (e.g., $\tau = (\phi - \theta)^{1/3} / \phi^2$) in MeBr gas-phase transport, where ϕ , θ , ρ_b , k_d , k_h , respectively, are the porosity, water content, bulk density, liquid-solid and liquid-gas partition coefficients and $\epsilon = \phi - \theta$. When the water content was increased from 0.058 to 0.180 $\text{cm}^3 \text{cm}^{-3}$, R_d increased from 1.21 to 1.58, τ decreased from 0.241 to 0.076 and the effective soil diffusion coefficient would be reduced by 76%.

In laboratory columns containing Greenfield sandy loam with 0.058 and 0.124 (cm^3/cm^3) volumetric water contents, the estimated loss after correcting for the presence of the column bottom was approximately 77% of the applied MeBr (See Table 4). When the water content was increased to 0.180 $\text{cm}^3 \text{cm}^{-3}$, only 62% was lost.

Table 4. Effects of Soil Type, Water Content and Bulk Density on MeBr Dissipation.

Treatment	Total Emissions (Measured) (%)	Total Degradation (%)	Mass Balance (%)	Total Emissions Corrected Using Diffusion Model (%)
Volumetric Water Content				
0.058	90	6	96	77
0.124	90	12	102	77
0.180	75	26	101	62
Bulk Density (g cm^{-3})				
1.40	90	12	102	77
1.70	64	29	93	53
Soil Type				
Greenfield SL	90	12	102	77
Carsetas LS	90	9	99	77
Linne CL	44	49	94	37

As the soil water content increased, the maximum MeBr flux density decreased and the time interval before reaching the maximum increased. Measurements of the MeBr gas concentration in the soil also indicated rapid movement through the soil column for the

drier soils. MeBr in these soil columns was completely depleted 54 and 72 h after the application. For the wetter soil, measurable concentrations remained in the column until 144 h after the application.

In a recent field experiment (Yates et al., 1994 unpublished data), lower MeBr emissions were observed for bare soil, deep application than for a tarped, shallow application in the same field. Part of this difference may have been attributed to the water content of the soil profile. During the deep-injection study, the average soil water content around the injection point (68 cm below the surface) was $0.223 \text{ (cm}^3/\text{cm}^3\text{)}$, whereas that observed during the shallow-injection study was $0.145 \text{ cm}^3/\text{cm}^3$. Yagi et al. (1.5) also attributed the decrease in MeBr emission from 87 in their first study to 34 % in their second study, in part, to soil moisture differences. Similar results were observed in the laboratory (3 7).

Soil Bulk Density. Soil bulk density can also have an effect on MeBr transport since the pore space decreases as bulk density increases. The bulk density, ρ_b , is related to the porosity from the relationship: $\text{porosity} = (1 - \rho_b/\rho_p)$, where ρ_p is the particle density.

In laboratory columns packed with Greenfield sandy loam, the corrected cumulative volatilization loss for a column with a bulk density of 1.70 g/cm^3 was 53%, significantly lower than the 77% loss from a column with a bulk density of 1.40 g/cm^3 . The columns with higher bulk density behaved in a manner similar to the wetter soil column described above. Measurable volatilization continued for 120 h, the maximum flux density was reduced from 9.7 to 3.9 mg/h/column compared to the low bulk density column, and the time to reach the maximum flux increased from 2.5 to 6.5 h after application.

In the untarped, deep-injection field study (Yates et al., 1994, unpublished data), the field was disced and packed with a tractor shortly (approximately 5 min) after MeBr was injected into the field. The disking and surface packing closed the openings above the injection fractures and increased the bulk density near the surface. This, along with a higher water content, probably contributed to the reduced total emission compared to the shallow-tarped experiment. In practice, packing the soil surface and carefully closing the soil fractures created during application also should be considered for minimizing MeBr volatilization.

Degradation. Along with volatilization of MeBr from the soil surface, hydrolysis and methylation are the principle degradative processes removing MeBr from agricultural soils (40,41). Gan et al. (41) investigated the effect of soil properties on MeBr degradation and sorption in several soils and estimated the degradation half-life for MeBr in Greenfield sandy loam to be approximately 8 to 27 d, decreasing with increasing soil depth.

Degradation affects volatilization since it removes MeBr from the soil; making it unavailable for transport to the atmosphere. The effect of soil organic matter on MeBr volatilization has been investigated in our laboratory for three soils. The Greenfield sandy loam has relatively low organic matter and clay contents and is representative of many soil types in the state of California. Carsetas loamy sand has a

very high sand content and very low organic matter and clay contents. Linne clay loam is relatively rich in organic matter and clay. Soil type had a pronounced effect on MeBr volatilization behavior as shown in Table 4. Volatilization of MeBr from untarped Carsetas and Greenfield soil columns following 30-cm injection was very rapid; both columns losing 77% of the applied MeBr. However, under the same conditions with the Linne clay loam, only 37% of the applied MeBr was lost. Analysis of Br^- concentration in soil at the end of the experiment revealed that 49% of the applied MeBr was degraded to Br^- in the Linne soil, while the degradation in Carsetas and Greenfield soils was approximately 10% (Table 4). The enhanced degradation of MeBr in Linne clay loam is likely due to its higher organic matter content (41-43).

Using a gas-phase diffusion model, it was predicted (35) that when the soil organic carbon content was increased from 2 to 4%, the MeBr emission rate decreased from 45 to 37% following a tarped (2 days), 25-cm application under the assumed conditions. However, in his simulation, only the effect of soil organic matter on adsorption behavior was considered. From the column experiments, it is clear that enhanced degradation due to higher organic matter content may play an important role in reducing MeBr volatilization in organic-matter-rich soils.

Pesticide Efficacy. Efficacy and the rate of application are important factors in the fate and transport of MeBr used in pest control. If new management methods are developed which enhance MeBr efficiency, the quantity used in agricultural settings can be reduced resulting in less MeBr leakage into the atmosphere. To assure high efficiency of MeBr use, however, the uniformity and efficacy of the application must be determined.

Measuring MeBr concentrations in the soil gas phase at different depths provides some of the information needed to determine efficacy. Shown in Figure 5 are soil gas concentrations from the bare soil, deep injection experiment described earlier.

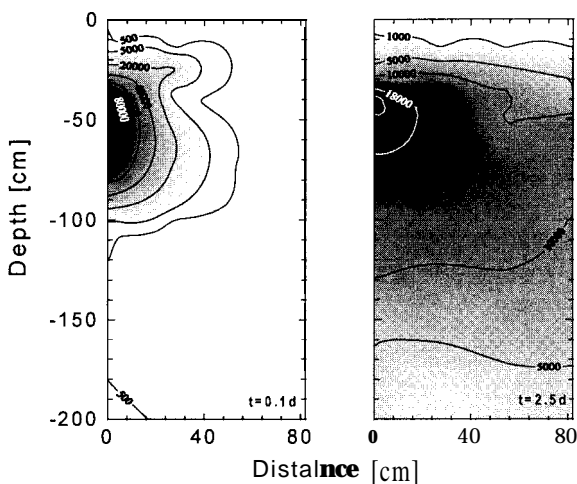


Figure 5. Soil gas concentrations at two times. Note: shading scales are different.

Initially, very high concentrations exist around the injection point. At later times, a more uniform concentration distribution occurs. This type of information is valuable to ensure that new management methods will be effective in controlling pests.

Deep placement of MeBr in coarse-textured soils is usually efficacious (44,45). Application to the heavy-textured subsoil may be less effective, particularly if the soil is saturated at that depth. Therefore, the depth to which MeBr may be actually injected is dependent on soil conditions and the distribution pattern of target organisms, and should be decided by weighing between the efficacy and emissions under certain circumstances. In recent plot-scale experiments (Yates et al., 1995, unpublished data) MeBr gas (e.g. hot-gas method) was injected at 60 cm depth and covered with 1.4-mil polyethylene or 1-mil Hytibar[®] films to investigate how various management factors affect MeBr emissions. Located 4 cm deep in each plot were bags containing citrus nematodes, *Rhizoctonia solani* fungi and yellow nutsedge seeds. When the soil was covered with polyethylene, poor efficacy was observed in deep-injection plots. When covered with the high-barrier plastic listed in Table 2, good pest control was observed.

Conclusions

The great variation among results of recent experiments measuring the total emission of MeBr from fields imply that many factors, including those related to application methods as well as to soil and climatic conditions, integratively influence MeBr transport and transformation in the soil-water-air system and hence its ultimate loss from the soil surface. It was found that variables related to application methods, e.g., injection depth and use of surface tarp, and soil properties, e.g., water content, bulk density, soil organic matter have pronounced effects on MeBr volatilization following soil injection (46,47).

The following conclusions can be drawn from this experimental information. Tarping consistently increased the residence time and amount of MeBr residing in the soil. The prolonged retention of MeBr in the soil resulted in more extensive degradation. Research indicates that the polyethylene film typically used for the surface cover is relatively permeable to MeBr and allows significant emissions compared to high-barrier plastic. This effect is more pronounced during periods of high temperature. Soil type, soil water content and bulk density are important factors affecting MeBr transport and transformation in soil, which ultimately affect volatilization. The total volatilization of MeBr from the organic-matter-rich Linne clay loam was only about half of that from a Carsetas loamy sand or a Greenfield sandy loam with relatively low organic matter contents. Organic matter additions which promote increased degradation offer another means for reducing volatilization. MeBr volatilization also decreased with increasing soil water content and bulk density. This dependence was mainly due to the reduced gas-phase diffusion as the result of reduced soil air porosity. Applying water at the soil surface can help to reduce volatilization losses.

To minimize volatilization, MeBr should be applied during periods of cool temperatures, relatively deep in organic-rich, moist soil under tarped conditions and the

soil surface packed immediately after the application. Depending on site-specific conditions, a new high-barrier plastic should be used. Injecting MeBr during periods of warm temperature, at a shallow depth in dry, loose soil without the use of plastic barriers will likely result in maximum volatilization rates and, therefore, should be discouraged. Before adopting any new emission-reduction technology, the pest-control characteristics of the new methodology needs to be tested in typical regions, soils and environmental conditions, Failure to do this may produce unacceptable levels of pest control.

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