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Department of Soil and Environmental Sciences, University of California, Riverside, California 92521, and Soil Physics and Pesticides Research Unit, USDA-ARS, U.S. Salinity Laboratory, 450 Big Springs Road, Riverside, California 92507

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JIANYING GAN,*^{,†} SCOTT R. YATES,* DONG WANG,* AND WILLIAM F. SPENCER+

Department of Soil and Environmental Sciences, University of California, Riverside, California 92521, and Soil Physics and Pesticides Research Unit, USDA-ARS, U.S. Salinity Laboratory, 450 Big Springs Road, Riverside, California 92507

Two currenttasks regarding the use of methyl bromide (MeBr) as a soil fumigant are to accurately estimate its volatilization rate into the atmosphere from soil fumigation and to develop application and soil management techniques that minimize this volatilization. In this study, we established experimentally that a series of soil factors, e.g., soil type, soil water content, and bulk density, affect MeBr behavior in the soilwater-air phases and its volatilization rate from the soil surface. Methyl bromide volatilization was significantly decreased in an organic matter-rich soil due to enhanced degradation and in moist and dense soils due to reduced diffusion in the gas phase. These results imply that MeBr volatilization rate may vary from one geographic region to another or from one field to another in the same region due to changes in soil conditions or even from one site to another in the same field due to soil heterogeneity. To minimize MeBr volatilization from soil, MeBr should be injected at great depths in moist soil under tarped conditions, with the soil surface packed before or immediately after the application. Applying MeBr at a shallow depth into relatively dry and loose soil under untarped conditions will result in maximum volatilization and therefore should always be avoided.

Introduction

Volatilization of methyl bromide (bromomethane, MeBr) into the atmosphere from its applications as a soil fumigant has reportedly contributed to the observed ozone depletion in the stratosphere (I-5). As a result of the Montreal Protocol and the Clean Air Act, actions are currently being undertaken to restrict the scale of MeBr production and use (6, 7). Over the last few years, research interest on MeBr has been primarily focused on two aspects. First, due to the many uncertainties regarding the sources of MeBr in the atmosphere, it is imperative to obtain more direct and accurate estimates of the contribution directly arising **from** man-made MeBr sources. Second, since MeBr is vital for the production of many crops, and currently there is no ideal alternative to replace it in soil sterilization, it is of great economic importance to develop innovative application and soil management strategies to minimize MeBr volatilization that would allow the scheduled phaseout of MeBr to be postponed or exemptions to be made.

Since soil fumigation consumes 80-85% of the manmade MeBr, volatilization during and after soil fumigation essentially controls the anthropogenic contributions. Determining MeBr volatilization rates from treated fields has been an active area of research for the last few years, and volatilization rates from 15 to 98% have been reported (8-13). The great variations among these measured volatilization rates imply that many factors, including those related to application methods as well as to soil and climatic conditions, integratively influenced MeBr transport and transformation in the soil-water-air system and hence its ultimate volatilization loss from the soil surface. In a previous study, it was found that variables related to application methods, e.g., injection depth and use of surface tarp, had pronounced effects on MeBr volatilization following soil injection (14). In this paper, the effect of three soil factors, i.e., soil type, soil water content, and bulk density, was determined and discussed. These factors have been known to influence the efficacy of MeBr fumigation (15,16), but their effect on MeBr atmospheric volatilization has not been experimentally examined.

Selection of these three soil factors is based on the transport mechanisms of MeBr in the soil-water-air environment. Due to its very low boiling point (3.4 °C at 1.0 atm) and extremely high vapor pressure (218 kPa or 1633 mmHg at 25 "C), MeBr transport in soil is mainly through its diffusion in the gas phase (17,18) **The transport** equation for gas phase concentration can be written as (19, 20)

$$\frac{\partial C_{\rm g}}{\partial t} = D_{\rm e} \frac{\partial^2 C_{\rm g}}{\partial x^2} - \mu C_{\rm g} \tag{1}$$

where C_g is the concentration in the soil gas phase (mg m⁻³); μ is the first-order degradation rate constant (d⁻¹), x is the distance (m), and D_e is the effective diffusion coefficient (m² d⁻¹) and is defined here as

$$D_{\rm e} \frac{D_{\rm s} K_{\rm H_{\rm m}}}{R_{\rm d}} \frac{\rho_{\rm b} K_{\rm d} + \theta + a K_{\rm H}}{\rho_{\rm b} K_{\rm d} + \theta + a K_{\rm H}}$$
(2)

where & is the retardation factor; θ is the volumetric water content ($cm^3 cm^{-3}$); ρ_b is the soil bulk density (g cm⁻³); a is the volumetric air porosity ($cm^3 cm^{-3}$); & is the linearized sorption distribution coefficient ($cm^3 g^{-1}$) between soil and water phases; and K_H is the dimensionless Henry's law constant. According to the Millington-Quirk equation (21), D_s is modified from the diffusion coefficient of the chemical in the air (D_g) by a gas tortuosity factor (ξ):

$$D_{\rm s} = \xi D_{\rm g} = \left(\frac{a^{10/3}}{\phi^2}\right) D_{\rm g} \tag{3}$$

where $\phi = a + \theta$ is soil total porosity.

^{*} Corresponding author telephone: (909)369-4&M; fax: (909)342-4964; e-mail address: jgan@ucracl.ucr.edu.

[†] University of California.

[‡] USDA-ARS.

TABLE 1 Some Characteristics of Soils Used

soi!*	organic matter (%)	cla (%)	y pH (H₂O)	surface area (m² g ⁻¹)	<i>K</i> d ^b (g cm ⁻³)	ρ _p ^c (g cm ⁻³)
Greenfield SL	0.92	9.5	7.4	14.4	0.10	2.67
Carsetas LS	0.22	0.1	7.2	2.0	0.04	2.40
Linne CL	2.99	25.1	6.0	19.6	0.10	1.91
^a SL, sandy loa	im; LS, Ioa	mysa	nd; CL,	clay loam.	^b K _d , exper	rimentally

determined adsorption coefficient of methyl bromide on moist soil. ${}^{\sigma}\rho_{\rm p}$, particle density in gcm⁻³.

In eqs 1 and 2, MeBr diffusion in the soil gas phase is proportional to D_s and inversely dependent on R_d . In eq 3, D_s or ξ decreases rapidly with decreases of a. Therefore, soil factors that influence one or more of the model parameters should also affect MeBr transport and its volatilization from the treated soil. Different soil types may have different μ , since MeBr degradation in soil was found to be highly dependent on soil organic matter content (22– 24). Different soils may also have different K_d or ρ_b . With the same soil, from eqs 2 and 3, increasing soil water content θ and bulk density ρ_b increases& and decreases D_{sr} resulting in reduced gas-phase diffusion.

Experimental Section

Soils. Three soils, Greenfield sandy loam (University of California Riverside Field Station, Moreno Valley, CA), Carsetas loamy sand (University of California Riverside Field Station, Coachella Valley, CA), and Linne clay loam (Santa Monica, CA), were taken from the 0- to the 30-cm depth in the field and after being air dried were passed through a 2-mm sieve before use. The characteristics of these soils are included in Table 1. Before packing into the columns, the air-dried soil was adjusted to a predetermined water content by adding deionized water and equilibrating for at least 24 h in closed containers to redistribute the moisture.

Closed, Packed Soil Column System. A closed, packed soil column system was developed and used in the current experiments (Figure 1). In brief, the system consisted of a packed soil column [62 (h) x 12.5 (i.d.) cm, bottom-sealed] and a sampling chamber of the same diameters [3.5 (h) x 12.5 (i.d.) cm, top-sealed], both made of glass. Soil with known water content was then packed carefully in 5-cm increments into the soil column to a predetermined bulk density. The sampling chamber was carefully sealed onto the soil column, and an air flow (I50 mL min⁻¹) was established through the inlet and outlet of the sampling chamber to sweep volatilized MeBr into sampling tubes containing activated coconut-based charcoal (ORBO-32 tubes, Supelco) installed at the outlets. Sampling ports, which were made by inserting Thermogreen septa (0.5 cm in diameter, Supelco) Into 0.4-cm openings in the column wall, were positioned every 10 cm along the column.

Columns were packed to different conditions for the different treatments (Table 2). For all the treatments, the soil surface was not covered with a tarp. To study the effect of soil type, the Greenfield and Carsetas soils were packed to a bulk density of 1.40 g cm⁻³ and a volumetric water content of approximately 0.120 cm³ cm⁻³. However, due to its high clay content, Linne clay loam was packed with a higher water content (0.274 cm³ cm⁻³) and a lower bulk density (1.21 g cm⁻³) to achieve a packing resembling the conditions in the field. The Greenfield sandy loam was the



FIGURE 1. Schematic diagram of the closed, packed soil column used in methyl bromide volatilization experiments.

TABLE 2

Characterization of Soil Columns Used for Methyl Bromide Transport and Emission Studies

treatment	soil	t	ype'	ρ	ь ^ь О ^с а	d R _d o	ξ Í
A-effect of soil type	Greenfield Carsetas L Linne CL	SL S	1.40 1.40 1.21	0.124 0.120 0.274	0.352 0.300 0.088	1.41 1.01 1.67	0.136 0.102 0.002
B-effect of soil moisture	Greenfield	SL	1.40	0.058	0.418	1.21	0.241
	Greenfield	SL	1.40	0.124	0.352	1.41	0.136
	Greenfield	SL	1.40	0.180	0.296	1.58	0.076
C-effect of	Greenfield	SL	1.40	0.124	0.352	1.41	0.136
bulkdensity	Greenfield	SL	1.70	0.146	0.217	1.48	0.047

^eSL, sandy loam; LS, loamy sand; CL, clay loam. ^b ρ_{b} , soil bulkdensity in g cm⁻³. ^c θ , soil volumetric water content in cm³ cm⁻³. ^d a, soil volumetric air content in cm³ cm⁻³. ^e R_d , retardation factor. ^f ξ , equals D_a/D_g .

only soil used for studying the effect of soil water content and bulk density. The water content range, 0.058-0.180 $cm^3 cm^{-3}$, used for determining the water content effect follows from the observed moisture regimes in the field where the soil was sampled. In **the** field during an untarped MeBr fumigation, soil water content varied from 0.05 cm³ cm⁻³ in the top surface layer (O-10 cm) to 0.176-0.284 cm³ cm⁻³ below the 30-cm depth (10). The bulk densities used in this study, 1.4 and 1.7 g cm⁻³, were also representative of the variation observed in the soil profile in the field, where soil bulk density increased from 1.35 g cm⁻³ in the surface layer to 1.65-1.7 g cm⁻³ below 30 cm (10).

Methyl Bromide Application and Sampling. For all the treatments, 40 mL of MeBr gas (3.9 mg mL⁻¹ at 1.0 atm and 25 °C) (Matheson Gas Products, Inc., East Rutherford, NJ) was injected 30 cm below the soil surface Into the packed soil columns via a sampling port using a gas-tight syringe. This rate is equivalent to about one-half of the typical field application rate of 200-300 kg ha⁻¹. The MeBr gas in the syringe was released into the soil within a few seconds at

the point approximately4.0 cm from the columnwall. The time that MeBr was injected into the soil was considered as time zero. Charcoal samplingtubes were changed every 0.5 h for the first 10 h after treatment and every 1.0 or 2.0 h thereafter except for the night hours between 11:30 P.M. and 7:30 A.M. when an 8-h interval was used. The number of tubes used was adjusted according to the sampling intervals; more tubes were used for longer intervals to eliminate breakthrough (25). Methyl bromide content in the sampling tubes was analyzed on a headspace-GC system, and MeBr volatilization fluxes in mg (MeBr) h^{-1} column⁻¹ were calculated. To follow MeBr spatial diffusion and dissipation in the soil column, at predetermined intervals, 0.5 mLof soil air was sampled at different positions along the column via the sampling ports, using a 1.0-mL push-button gas-tight syringe. The air samples were transferred into 21-mL headspace vials, and the vials were crimp sealed with aluminum seals and Teflon-faced butylrubber septa (Supelco). Methyl bromide concentration in the vials was determined on the headspace-GC system. Monitoring of MeBr volatilization was continued until MeBr in the charcoal sampling tubes became no longer detectable. Upon termination, soil was sampled from different depths, and Br⁻ concentration, soil water content, and bulk density were determined. Increases in Br⁻ concentration in the soil at the end of the experiment was used to estimate the proportion of MeBr degraded.

Analysis of Methyl Bromide and Br-. Detailed procedures for analyzing MeBr in charcoal sample tubes and soil air samples on a headspace-GC system were reported elsewhere (26). In brief, charcoal containing MeBr in the ORB0 tubes was pushed into headspace vials (Tekmar Co., Cincinnati, OH), and after 1.0 mL of benzyl alcohol was added, the vials were immediately sealed with aluminum caps and Teflon-faced septa. These sample vials were then equilibrated at 110 °C for 15 mln in a Tekmar 7000 headspace autosampler (Tekmar Co., Cincinnati, OH), and 1.0 mL of the headspace vapor was introduced to the injection port of a Hewlett Packard HP 5890 GC equipped with an electron capture detector. GC conditions were RTX-624 Crossbond cyanopropylphenyl methyl polysiloxane phased capillary column (30 m x 0.25 mm x 1.4 μ m), 1.1 mL min⁻¹ of helium flow rate, 20:1 split ratio, 170 °C inlet temperature, 35 °C isothermal oven temperature, and 240 °C detector temperature. Calibration curves were made by analyzing charcoal tubes spiked with known amounts of MeBr gas (0.2-2000 μ L) under the same conditions. Closed headspace vials containing soil air samples were also analyzed on the headspace-GC under the same conditions except no solvent was added into the vials. Calibrations curves were made by analyzing vials containing known amounts of MeBr gas $(0.01-6.0 \mu L)$ under the same conditions. Bromide ion concentration in soil was determined on a QuikChem AE automated ion analyzer (LaChat, Milwaukee, WI) following extraction with deionized water.

Results and Discussion

Effect of Soil Type on Methyl Bromide Volatilization. Greeniield sandy loam, which has relatively low organic matter and clay contents, 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 (Table 1). As seen in Figure 2, soil type had a pronounced effect on MeBr volatilization behavior.



Time after application (h)

FIGURE 2 Effect of soil type on methyl bromide volatilization. (a) Volatilization flux in mgh^{-1} column-' and (b) accumulative volatilization rate in percent of applied.

Volatilization of MeBr from untarped Carsetas and Greenfield soils following 30-cm injection was almost instantaneous, and MeBr in the soil became depleted shortly after the application. The maximum volatilization flux occurred 2.0-2.5 h after the injection, at a rate of 9.7-14.8 mg h^{-1} column⁻¹ (Figure 2a). The cumulative volatilization losses were 89% and 90% from Carsetas and Greenfield soils, respectively (Figure 2b). However, with the Lirme clav loam under the same conditions, only 44% of the applied MeBr was emitted via volatilization. The maximum volatilization flux appeared 7.5 h after application at a rate of only 2.4 mg h^{-1} column-i. 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 Greenfleld soils was approximately 10% (Table 3). The enhanced degradation of MeBr in Linne clay loam is likely due to its higher organic matter content as indicated in earlier work (22-241.

As depicted by MeBr concentration profiles in the soil air, in the columns packed with Carsetas loamy sand and Greenfield sandy loam, MeBr diffused rapidly in both directions away from the injection point (30 cm from the surface) immediately after application (Figure 3). Since there was no surface cover, MeBr volatilized rapidly into the air from the soil surface and became nondetectable in the soil air shortly after application. In Linne soil, MeBr was apparently more confined to the region of application within the first few hours, but also dissipated rather rapidly from the soil column, partly because of the enhanced MeBr degradation in this soil (Figure 3).

TABLE 3 Methyl Bromide Volatilization loss, Degradation, and Mass Recovery under Various Soil Conditions"

treatment	volatilized (%) (measured)	d e g raded (%)	mass recovered º (%)	volatilized (%) (corrected) ^b
soil type				
Greenfield SL	90	12	102	77
Carsetas LS	89	9	99	77
Linne CL	44	49	94	37
moisture (cm ³ cm ⁻³)				
0.058	90	8	96	77
0.124	90	12	102	77
0.180	75	26	101	62
density (gcm ⁻³)				
1.40	90	12	102	77
1.70	64	29	93	53

^e All values are in percent of applied MeBr(156 mg column-'). ^b Volatilization rates extrapolated to infinite depth.



FIGURE 3. Distribution of methyl bromide in soil air after 30-cm injections in different soils. (a) Carsetas loamy sand; (b) Greenfield sandy loam; and (c) Linne clay loam.

It must be noted that the application method used in this **study differs** from the standard means of injecting MeBr as a pressurized liquid and may affect MeBr distribution in soil at the very early stage. After liquid MeBr is injected, it absorbs heat from the surrounding environment, and MeBr vaporizes within minutes into the soil air. In this study, right after injection, MeBr existed likely as an expanded spheric source, with a diameter at least 6-8 cm, assuming that the gaseous MeBr displaced the soil air around the injection point. Given the relatively small diameter of the soil column (12.5 cm), shortly after the injection, MeBr movement can be assumed to be onedimensional. In the field following a standard injection, MeBr was introduced as line sources spacing about 20-30 cm apart for shallower applications. The initial diffusion of MeBr in this situation may be regarded as twodimensional but shortly **becomes** one-dimensional as MeBr between adjacent line sources reached equilibrium due to decompression and diffusion.

Assuming that the Henry's law constant for MeBr $K_{\rm H}$ is 0.25 at 25 °C, the total MeBr inventory in the soil-waterair phases was calculated from the measured MeBr concentration in the gas phase and the $K_{\rm d}$ values (Table 1) using the following relationship:

$$M = C_{\rm a}aV + \frac{C_{\rm a}}{K_{\rm H}}\theta V + \frac{K_{\rm d}C_{\rm a}}{K_{\rm H}} \left(\frac{\rho_{\rm b}}{\rho_{\rm p}}V\right) \tag{4}$$

where *M* is the total MeBr amount remaining in all the three phases; C_a is the measured MeBr concentration in the soil air; Vis the total volume of the soil column (7,360 cm³); ρ_p is soil particle density in g cm⁻³ (Table 1); and a, θ , ρ_b , K_H , and K_d are as given above. Under experimental conditions, at equilibrium, the fractions of MeBr in the air, water, and solid phases were respectively 33,47, and 20% for the Greenfield sandy loam; 35,56, and 9% for the Carsetas loamy sand; and 7, 80, and 13% for the Linne clay loam. The retardation factor (R_d) and tortuosity ξ of MeBr gasphase diffusion in these soils under the experimental conditions were calculated from eqs 2 and 3 (Table 2). In the Greenfield and Carsetas soils, since a significant fraction of the total MeBr was in the gas phase, MeBr gas-phase diffusion was predominant, resulting In rapid volatilization of MeBr from the soil columns (Figure 4a). For instance, 24 h after application, only 18 and 27% of the applied MeBr remained in the soil, while 81 and 72% were lost via volatilization for the Carsetas and Greenfield soil columns, respectively. In Linne soil, the calculated R_g is greater, and ξ is significantly smaller than that in the other two soils (Table 2). From the gas-phase transport model, MeBr diffusion in the gas phase of this soil should be greatly reduced. Restricted gas-phase diffusion and enhanced degradation collectively contributed to the lower volatilization rate of MeBr from the column packed with the Linne soil (Figure 2).

Since soil columns used in this study were sealed at the bottom, downward diffusion of MeBr was restricted to 60 cm below the surface; this resulted in overestimated volatilization rates that were corrected using diffusion models. In brief, extrapolating column measurements to infinite depth involved three steps: First, multiple sets of the measured MeBr concentrations in soil air were fitted to the described vapor transport model (eq 1) to obtain model parameters under experimental conditions. The same parameters were then used in the same model to estimate MeBr volatilization rates for infinite depth scenarios. Finally, a correction factor, i.e., the ratio of the estimated value over the measured value was calculated and used to extrapolate the measured volatilization rates to infinite depth conditions. After correction to infinite depth, the emission rate from the Linne clay loam was only 37%, significantly less than the corrected emission rate of approximately 77% from the other two soils (Table 3). Using



FIGURE 4. Dissipation of total methyl bromide from soil columns. (a) Effect of soil type; (b) effect of soil water content; and (c) effect of soil bulk density.

a gas-phase diffusion model, Reible (*18*) predicted that, when soil organic carbon content was increased from 2 to **4%, MeBr** emission rate decreased from 45 to 37% following a **tarped** (2 d), **25-cm** application under the assumed conditions. However, in his simulation, only the effect of soil organic matter on adsorption behavior was considered. From this study, 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.

Since **MeBr** is used worldwide, many different soil types may be involved. The dependence of **MeBr** volatilization on soil type should be considered when estimating the contribution of agricultural fumigation operations to the total atmospheric **MeBr**. The few **MeBr** emission rates measured under field conditions cannot be extended without modification for other soil types, particularly for soils with high organic matter content.

Effect of Soil Water Content on Methyl Bromide Volatilization. Approximately 90% of the injected MeBr was emitted from the columns packed with Greenfield sandy loam at 0.058 and 0.124 cm³ cm⁻³ volumetric water contents, but only 75% was lost from the same soil packed at 0.180 cm³ cm⁻³ water content (Figure 5). With increases in soil



FIGURE5. Effectofsoilwatercorrtenton methyl bromidevolatilization fmm Greenfield sandy loam. (a) Volatilization flux in mg h^{-1} column.' and (b) accumulative volatilization rate.

water content, the maximum volatilization flux decreased, and the time to reach the maximum flux was delayed (Figure 5a). This effect of water content on MeBr volatilization can be explained by the interactions of soil water content and the retardation (R_d) and tortuosity (ξ) factors in MeBr gas-phase transport. When the water content was increased from 0.058 to $\hat{0}$.180 cm³ cm⁻³, R_d increased from 1.21 to 1.58, and ξ decreased from 0.241 to 0.076. Methyl bromide concentrations in the soil gas phase indicated that MeBr diffused rapidly throughout the soil column in the drier soils and volatilized from the untarped soil surface (Figure 6a,b) Methyl bromide in the soil columns was completely depleted 54 and 72 h after the application. In the soil with a θ of 0.180, MeBr was found to be more concentrated around the injection point for the first few hours, and MeBr concentration in the column did not approach the detection limit until 144 h after the application (Figure 6c). The calculated total MeBr remaining in soil increased with increasing soil water content (Figure 4b). For instance, at 24 h after application, 7,27, and 44% of the applied 156 mg of MeBr remained in the column for the water contents of 0.058, 0.124, and 0.180 cm³ cm⁻³, respectively. The increased retention of MeBr in the moist soil should result in more extensive degradation to Br-. This was confirmed with the measurement of Br⁻ concentration at the end of the experiment (Table 3). The enhanced degradation in moist soils was a result of reduced MeBr diffusion and extended retention in soil rather than of increased MeBr hydrolysis caused by the higher water content. Methyl bromide degradation in soil was found not to be affected by water content in an incubation experiment (15) Methyl



FIGURE 6. Distribution of methyl bromide in soil air after 30-cm injections in soil with different water contents: (a) $0.058 \text{ cm}^3 \text{ cm}^2$; (b) $0.124 \text{ cm}^3 \text{ cm}^{-3}$, and (c) $0.180 \text{ cm}^3 \text{ cm}^{-3}$.

bromide volatilization rates after correction for depth restriction were 77, 77, and 62% for the water contents of 0.058, 0.124, and 0.180 g cm⁻³, respectively (**Table** 3). The lesser MeBr emissions observed for an untarped deep application than a tarped shallow application in the same field may be partially attributed to the different water contents in the soil profile (10, 12). During the deep-injection study, the averaged soil water content around the injection point (68 cm below the surface) was 0.223 cm³ cm-s, which is considerably higher than that during the shallow-injection study (0.145 cm³ cm⁻³). Though the measured water content data were not given, Yagi et al. (9) also attributed the decrease of 87 to 34% in MeBr emission in their second study partly to soil moisture differences.

To minimize MeBr volatilization, soil water content can be altered before or immediately after fumigation. In practice, among all the soil factors, increasing soil water content is relatively easy and economically feasible. In theory, from eq 3, when soil is saturated with water, that is, when a = 0, MeBr diffusion in the gas phase will be completely stopped, and transport will occur via liquid diffusion, which is 4 orders of magnitude slower than the gas-phase diffusion (19). Surface irrigation coupled with coveringthe soil with a tarp was demonstrated to be effective in preventing MeBr from leaving the treated soil under



Time after application (h)

FIGURE 7. Effect 0^{f} soil bulk density on methyl bromide volatilization from Greenfield sandy loam. (a) Volatilization flux in mg h^{-1} column⁻¹ and (b) accumulative volatilization rates.

laboratory conditions (17). However, it must be realized that sufficient diffusion of the fumigant in the soil is essential for achieving adequate efficacy. Consequently, soil water content in the target zone will need to be maintained below a certain value. Effect of high soil water content on MeBr efficacy in controlling nematodes and pathogens should be further studied.

Effect of Soil Bulk Density on Methyl Bromide Volatilization. Cumulative volatilization loss of MeBr from the column packed with Greenfield sandy loam at 1.70 g cm⁻³ was 64%, which was significantly lower than the loss of 90% from the same soil packed at a lower bulk density, 1.40 $g \text{ cm}^{-3}$ (Figure 7). In the denser soil column, detectable volatilization continued for 120 h, with the maximum volatilization flux reduced from 9.7 to 3.9 mg h⁻¹ column⁻¹ and the time to reach the maximum flux delayed from 2.5 to 6.5 h after application (Figure 7a). Soil bulk density affected MeBr volatilization behavior mainly via affecting the tortuosity (ξ) and retardation (R_d) factors for the gasphase diffusion of MeBr. When soil bulk density was changed from 1.40 to I.70 g cm⁻³, R_d increased from 1.41 to 1.48, and ξ decreased from 0.136 to 0.047. Analysis of MeBr in the soil gas phase showed that MeBr diffusion was slower and that MeBr was retained significantly longer in the denser column (Figure 8). Total MeBr remaining in the three phases in the dense column declined more gradually For example, at 24 h, 49 and 27% of the applied MeBr remained in the columns at 1.70 and 1.40 g cm⁻³, respectively (Figure 4c). Reduced volatilization rate of MeBr from the more dense soil column coincided with more extensive degradation (Table 3). The proportion of MeBr



MeBr concentration in soil air (mg L⁻)

FIGURE 8. Distribution of methyl bromide in soil air after 30-cm injections in soil with different bulk densities: (a) 1.40 g cm⁻³ and (b) 1.70 g cm⁻³.

degraded to **Br**⁻ in the denser soil was 2.5 times that in the lesser dense soil. The volatilization rates after correction for the restricted lower boundary conditions were 77 and 53% for the bulk densities of 1.40 and 1.70 g cm⁻³. respectively (Table 3).

In the untarped, deep-injection field study (12), the field was packed with a tractor shortly after MeBr was applied into the field. Surface packing closed the openings above the injection paths and increased the bulk density near the surface and therefore may also have contributed to the reduced emission. In practice, packing the soil surface and carefully closing the trench openings along the injection paths after application should be also considered for mmimizmg MeBr volatilization Injecting at a greater depth where soil is denser is another approach suggested by the dependence of MeBr behavior on soil bulk density.

It must be pointed out that, in this study, even after extrapolating the measured rates to infinite depth, the corrected estimates cannot be directly related to field conditions due to many simplifications. Many processes and factors that may or may not significantly affect MeBr behavior were not considered in this experimental simulation approach. For instance, in this study soils were sieved and homogeneously packed; air flow rates across soil surfaces were much smaller than the normal wind velocity in the field; MeBr was injected as a gas rather than in a liquid form; and factors such as temperature and humidity were controlled rather than varied. Nevertheless, under laboratory conditions, since individual factors were precisely controlled, the contribution of each factor could be quantitatively determined. This information is difficult to obtain in the field where numerous processes and factors are simultaneously involved, and it is important for interpreting field observations as well as for providing the rationale for developing emission-reduction techniques.

As shown in this study, soil type, soil water content, and bulk density all had significant influences on the MeBr transport and transformation behavior in the soil-waterair phases and the ultimate volatilization from soil surfaces. The total volatilization of MeBr from the organic matterrich I&me clay loam was only about half of that from a Carsetas loamy sand or a Greenfield sandy loam with relatively low organic matter contents. Since MeBr is used worldwide and soils of various characteristics are involved, the dependence of MeBr volatilization rate on soil types should be considered when obtaining estimates for the atmospheric input originating from fumigated agricultural fields. Methyl bromide volatilization also decreased with increasing soil water content and bulk density, and this dependence was mainly due to the reduced gas-phase diffusion as the result of reduced soil air porosity. Data from this study and a separate study on the effect of application methods indicate that many application method- and soil-related factors affect MeBr volatilization. Consequently, unless the experimental conditions are thoroughly characterized and documented, it is difficult or impossible to interpret and compare field measured emission rates. For the same reason, there does not exist a single emission rate that is representative for different conditions. To minimize volatilization, MeBr should be applied at a deep position in moist soil under tarped conditions, with the soil surface packed immediately after the application. Injecting MeBr at a shallow depth in dry, loose soil under untarped conditions will result in maximum volatilization rates and therefore should be always discouraged.

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