Volatilization and Distribution of Methyl Iodide and Methyl Bromide after Subsoil Application

J. Gan,* S. R. Yates, H. D. Ohr, and J. J. Sims

ABSTRACT

Methyl iodide (MeI) was recently proposed as a potential replacement for methyl bromide (MeBr) as a soil fumigant, but little is known about its fate in the environment. Volatilization of MeI was measured and compared with that of MeBr in packed soil columns with different soils and under various soil surface conditions. Under the same conditions, MeI volatilization loss was greater than that of MeBr, and the enhanced volatilization was attributed to its slower degradation in soil. In a Greenfield sandy loam (coarse-loamy, mixed, thermic Typic Haploxeralfs), the greatest loss occurred in a nontarped application (78% for MeI and 62% for MeBr), with the smallest loss in a high-barrier plastic-tarped treatment (28% for MeI and 24% for MeBr). Covering the soil surface with polyethylene film was ineffective in preventing MeI or MeBr volatilization. Volatilization losses of MeI and MeBr were also influenced by soil type, and were significantly less from soils that were high in organic matter content and capable of rapidly degrading the fumigants. Ten days after a point application (30 cm) in field plots covered with polyethylene film, higher MeI concentrations were detected at most depths. Because of its longer persistence in soil, MeI may have a greater tendency to reach groundwater than MeBr.

Because of its ozone-depleting nature, MeBr (bromomethane, MeBr), the currently most widely used soil fumigant, will be banned by the year 2001 in the USA, and at a later time in the rest of the world (USEPA, 1993; The United Nations Environment Programme, 1995). Alternative fumigants or fumigation techniques are urgently needed to substitute for MeBr to control soilborne pests (The National Agricultural Pesticide Impact Assessment Program, 1993; Ferguson and Padula, 1994). Methyl iodide (iodomethane, MeI) was recently proposed as a direct replacement for MeBr (Ohr et al., 1996). One distinguishing advantage that MeI possesses over MeBr is that MeI has a very short atmospheric life time (4–8 d, compared with 1.5–2.0 yr for MeBr), and therefore is unlikely to reach the stratosphere to contribute to ozone depletion (Solomon et al., 1994; Ohr et al., 1996). In several greenhouse and field-efficacy tests, MeI was consistently found to be more or at least equally active as MeBr in controlling selected parasitic nematodes, weeds, insects, bacteria, and fungi (Sims et al., 1995; Ohr et al., 1996; Becker et al., 1997; Zhang et al., 1997). However, since MeI is not a registered pesticide, many aspects of its behavior in the soil-water-air environment are unknown. Before much more effort is invested to develop this chemical into a commercial fumigant, information is needed on a few fundamental processes, for example, transport and transformation, and the potential for causing air or groundwater contamination.

MeI has a time-weighted threshold concentration for human exposure in air of 2 ppm (ACGIH, 1994). Excessive discharge of MeI into the air during fumigation may therefore be hazardous to field workers or nearby residents. MeI has a moderate toxicity (subcutaneous LD_{50} in mice = 110 mg kg^{-1}, Kutob and Plaa, 1962), and was once a suspected carcinogen (International Agency for Research of Cancer, 1986). Contamination of groundwater with MeI, particularly at sites where the groundwater table is high, may be another concern. Knowledge of MeI transport and distribution in the soil profile is also necessary for the design of optimal application methods that will allow the use of a minimum amount of chemical while achieving sufficient control. As the efficacy of a fumigant generally correlates well with its distribution patterns in soil (Kolbezen et al., 1974; McKenry and Thomason, 1974), measures that maximize concentrations in the pest-infested zones will likely lead to better control. As found for MeBr and a few other fumigants, several application and soil-related variables, for example, use of surface cover, change of injection depth and water management, may be modified to maximize a fumigant's effectiveness while reducing its environmental risk (Reible, 1994; Jin and Jury, 1995; Gan et al., 1996, 1997).

We have conducted a series of studies to compare MeI and MeBr transformations and transport after soil application. Methyl bromide was used as a reference chemical in these studies because it is structurally analogous to MeI, and in addition, many aspects of its behavior are already well understood. In a previous study, MeI was shown to degrade significantly more slowly than MeBr in soil, and under the same conditions, the partition of MeI from air into water or from water into soil was slightly greater than that of MeBr (Gan and Yates, 1996). From these differences, and the difference in their vapor pressures and boiling points, atmospheric volatilization losses and soil distribution patterns of MeI can be expected to be different from those of MeBr following similar applications.

In this study, we used packed soil columns and field plots to determine the difference between MeI and MeBr in atmospheric volatilization and soil distribution. In the column experiments, effect of surface cover was studied by using three surface conditions, nontarped, polyethylene film-tarped, and high-barrier film-tarped. To assess the effect of soil type, volatilization and distribution of MeI and MeBr were also determined in four different soils, ranging from an organic matter-rich potting mix to an organic matter-poor sandy loam. In the

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Abbreviations: MeI, methyl iodide; MeBr, methyl bromide; PE, polyethylene film; HDPE, high-density polyethylene film; HB, high-barrier film; SL, sandy loam; CL, clay loam; LS, loamy sand.

field, vertical movement of MeI and MeBr in polyethylene tarped field plots was followed from 0 to 270 cm after a point application at 30 cm, and differences in downward penetration and concentration profiles between the two chemicals were compared.

MATERIALS AND METHODS

Chemicals and Soils

Methyl iodide (Aldrich Chemical Co., St. Louis, MO) and MeBr (Matheson Gas Products Inc., East Rutherford, NJ) both had a purity of 99.5%. Before use, gaseous MeBr was chilled to liquid MeBr with dry ice and then kept at −15°C. The density of liquid MeBr was 1.73 g mL^{-1}, and that of MeI was 2.28 g mL^{-1}.

A Greenfield sandy loam (SL, OM = 0.92%), a Carsitas loamy sand (mixed, hyperthermic Typic Torripsamments) (LS, OM = 2.51%), a Linne clay loam (fine-loamy, mixed, thermic calcic Pachic Haploxerolls) (CL, OM = 2.99%), and a nursery potting mix (1:1 mix of topsoil and fir sawdust, OM = 9.60%) were used in the column experiments. Other properties of these soils were given elsewhere (Gan and Yates, 1996). The soil in the field plots was an Arlington SL, that contained 1.3% organic matter in the top 30 cm, but decreased to <0.5% below 60 cm. For laboratory studies, moist soils were passed through a 2-mm sieve without air drying, and the final water content was adjusted to 12% for Greenfield SL and Carsitas LS, and 18% for the nursery potting mix and Linne CL. A higher water content was used for the latter two soils because of their higher clay or organic matter contents.

Plastic Films

Two types of plastic films, 1.4 mil (0.035 mm) high-density polyethylene film (HDPE) (TriCal Co., Hollister, CA) and a high-barrier film, Hyti-bar, (donated by Klerk's Plastic, Belgium), were used in determining the effect of surface cover. The diffusion coefficient, in mmol m^{-2} h^{-1} under 1 mmol L^{-1} concentration difference across the membrane at 20°C, was determined to be 7.6 ± 0.3 and 8.9 (± 0.3) for MeBr and MeI, respectively, through the HDPE film, and 0.08 ± 0.03 and 0.06 ± 0.02, respectively, through the high-barrier film (Yates et al., 1997). The film used on field plots was 4-mil (0.1 mm) polyethylene film, and the measured diffusion coefficient was 2.2 ± 0.3 and 1.8 ± 0.2 mmol m^2 h^{-1} for MeI and MeBr, respectively.

Volatilization and Vapor Transport in Packed Soil Columns

A closed, packed soil column system was used to measure volatilization losses and vapor phase transport of MeI and MeBr under controlled conditions. Detailed descriptions of the column system and sampling procedures were given elsewhere (Gan et al., 1996, 1997). In brief, the sieved moist soil was packed into a closed-bottom, 62 cm high by 12.5 cm (i.d.) glass column to a predetermined bulk density and volumetric soil water and air contents. A sampling chamber [4 cm high by 12.5 cm (i.d.), top-sealed] was sealed onto the soil column, and an airflow of 150 mL min^{-1} above the soil surface was used to sweep the volatilized fumigant into a charcoal sampling tube (ORBO-32, Supelco., Bellefonte, PA). This flow rate did not create a significant negative pressure across the soil surface that might induce convective movement of fumigants in soil vapor phase. Septum-sealed sampling ports were spaced in incremental distances along the soil column to allow soil gas to be sampled at different depths. With the tarped treatments, a piece of the selected plastic film was placed between the soil column and the sampling chamber, and the connection carefully sealed. In this system, the loss of applied fumigant occurs only via volatilization from the surface or degradation in the soil column.

Conditions of the packed columns used in this study are given in Table 1. To determine the effect of surface cover, columns packed with the Greenfield SL were either not covered (nontarped), covered with the HDPE film (PE-tarped), or covered with the high-barrier film (HB-tarped). To study the effect of soil type, columns were packed with the Greenfield SL, Carsitas LS, Linne CL or the nursery potting mix, and all columns were covered with the polyethylene film. For the potting mix and Linne CL, due to their high organic matter content or clay content, lower bulk density and higher water content had to be used to achieve field-like packing (Table 1).

For all the treatments, application of fumigants was made by simultaneously injecting 85 μL of MeI (194 mg) and 110 μL of liquid MeBr (190 mg) into the same soil column. The chemicals were delivered at the center of the column via the gas sampling port 30 cm below the soil surface. These application rates were equivalent to ≈110 kg ha^{-1} (100 lb $acre^{-1}$) for both fumigants. The time that MeI and MeBr were injected was considered as time zero. After application, sample tubes were periodically changed, and MeI and MeBr in the sample tubes were analyzed on a Tekmar 7000 Headspace Autosampler in tandem with an HP 5890 GC equipped with an ECD, using a reported method (Gan et al., 1995). The conditions for the headspace autosampler were: equilibration temperature, 90°C; equilibration time, 10 min; and sample loop, 100 μL. The conditions for the GC were: RTX-624 capillary column (30 m by 0.25 mm by 1.4 μm, Restek Corp., Bellefonte, PA); column flow rate 1.7 mL min^{-1} (He); oven temperature 40°C; injection port temperature 170°C; and detector temperature 240°C. Under these conditions, MeBr was eluted at 2.5 min, and MeI at 4.0 min. Volatilization fluxes were calculated as milligrams per hour per column, and the cumulative volatilization losses, in percentage of applied chemical, were obtained by integrating volatilization fluxes over sampling time.

Table 1. Characterization of soil columns used for methyl iodide (MeI) and methyl bromide (MeBr) transport and volatilization studies and estimated diffusion coefficients D_s (cm^2 d^{-1}) for each column.†

Treatment	Soil type‡	Surface§	ρ_b, g cm^{-3}	θ, m^3 m^{-3}	a, m^3 m^{-3}	D_s, MeI	D_s, MeBr
Effect of surface cover	Greenfield SL	Nontarped	1.45	0.21	0.29	300	420
	Greenfield SL	PE-tarped	1.45	0.21	0.29	270	530
	Greenfield SL	HB-tarped	1.45	0.21	0.29	245	550
Effect of soil type	Greenfield SL	PE-tarped	1.45	0.21	0.29	270	530
	Carsitas LS	PE-tarped	1.45	0.17	0.29	530	810
	Linne CL	PE-tarped	1.16	0.21	0.32	680	1010
	Potting Mix	PE-tarped	1.14	0.21	0.29	300	630

† ρ_b, soil bulk density; θ, volumetric soil water content; a, volumetric soil air content.
‡ SL = sandy loam; LS = loamy sand; CL = clay loam.
§ PE = polyethylene film; HB = High-barrier film.

At different time intervals, 0.5 mL of soil air was withdrawn using a gastight syringe via the septa at different depths along the column. Soil air in the syringe was quickly transferred into 9-mL headspace vials, and the vials were immediately capped with aluminum seals and Teflon-faced butyl rubber septa. The sealed sample vials were analyzed for MeI and MeBr content on the headspace-GC system under the same conditions given above.

Extrapolation of Laboratory Measured Volatilization Losses

Since the closed column bottom prevented MeI or MeBr from diffusing below 60 cm in the soil columns, such laboratory column measurements overestimate fumigant volatilization losses compared with the field situation. An extrapolation method based on a transport model was used to correct the lower boundary effect and extrapolate the measured volatilization rates to an analogous field situation; that is, with an infinite lower boundary condition (Gan et al., 1996). In brief, multiple series of measured soil gas concentrations at different depths were fitted into a vapor transport model based on Ficks law to obtain model parameters, using the boundary conditions appropriate for the experiment. These parameters were then used in the same model to estimate volatilization losses for an infinite lower boundary condition. Though two components (i.e., MeI and MeBr) were present in the same column, since their mole fractions in soil air were very low (except for the very initial period of time when liquid source still existed), Ficks law is believed to be adequate for describing transport (Leffelaar, 1987; Amali and Rolston, 1993). Similar experimental setup and model extrapolation procedures were used previously in determining MeBr volatilization losses under various management regimes to give estimated values close to field observations (Gan et al., 1996, 1997).

Field Plot Experiments

Distribution of MeI and MeBr in the soil profile following 30-cm tarped applications was determined in 3 by 3 m plots in a field next to the Univ. of California, Riverside Campus in September 1996. Soil water content at the time of fumigation was from 1.1 to 3.4% for the top 45 cm, and averaged 7.5% from 45 to 200 cm. The average air temperature during the experiment was 21.7°C, with the average daily high at 30.2°C, and the average daily low at 15.6°C.

In the field plots, a hole 6 cm in diameter was augured 15 cm from the center point, and a soil gas sampling probe was carefully installed in the hole. The sampling probe allowed soil air to be sampled from the following depths: 0, 15, 25, 60, 90, 180, and 270 cm. The design of the sampling probe was described in detail by Kolbezen et al. (1974). The plots were pre-tarped with 4-mil (0.1 mm) polyethylene film, with the edges of the plastic buried ≈15 cm into the soil. Before fumigant application, a piece of Teflon tubing was installed at the center of the plot, with one end buried 30 cm below the surface and the other end aboveground. To apply MeBr, 100 g MeBr in a crimp-sealed serum bottle was chilled overnight on dry ice, and a double-ended hollowed needle was first forced into the open end of Teflon tubing and then pierced through the septum on the serum bottle. When the bottle was inverted, MeBr was quickly forced into the soil under pressure. To apply MeI, 100 g MeI was directly injected with a syringe through the Teflon tubing into the soil. Three plots were treated with each fumigant.

At different time intervals after application, known volumes of soil air (20 or 40 mL) were withdrawn from the sampling probes using a 60-mL syringe. The sample was passed through a charcoal sampling tube (ORBO-32, Supelco), and MeBr or MeI was adsorbed on the activated C. Methyl bromide in the charcoal tubes was determined on the headspace-GC system under the conditions given above. Due to the high sensitivity of MeI on ECD, the charcoal from MeI sample tubes was extracted with 4 mL hexane in a closed 9-mL vial, and a 2 μL aliquot was injected into the GC after dilution. The concentrations were calculated as mg L^{-1} of soil air.

RESULTS AND DISCUSSION

Volatilization from a Sandy Loam under Various Surface Conditions

The MeI and MeBr volatilization fluxes and cumulative volatilization losses following 30-cm deep application in the Greenfield SL under nontarped, polyethylene film-tarped, or Hyti-bar film-tarped conditions are shown in Fig. 1 and 2. The same column system and sampling procedures were used in previous studies to determine MeBr emissions under various application and soil conditions, and highly reproducible measure-

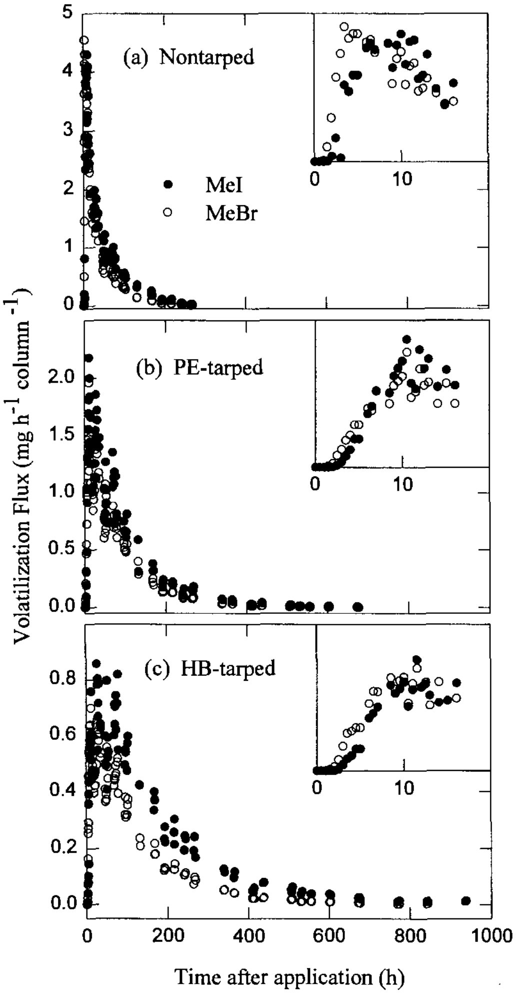

Fig. 1. Volatilization fluxes of methyl iodide and methyl bromide from a Greenfield sandy loam in 60-cm packed soil columns when soil surface was (*a*) nontarped; (*b*) tarped with 0.03-mm polyethylene film; and (*c*) tarped with Hyti-bar film. Application of both chemicals was at the 30-cm depth. Inserts show fluxes for the initial 20 h after application.

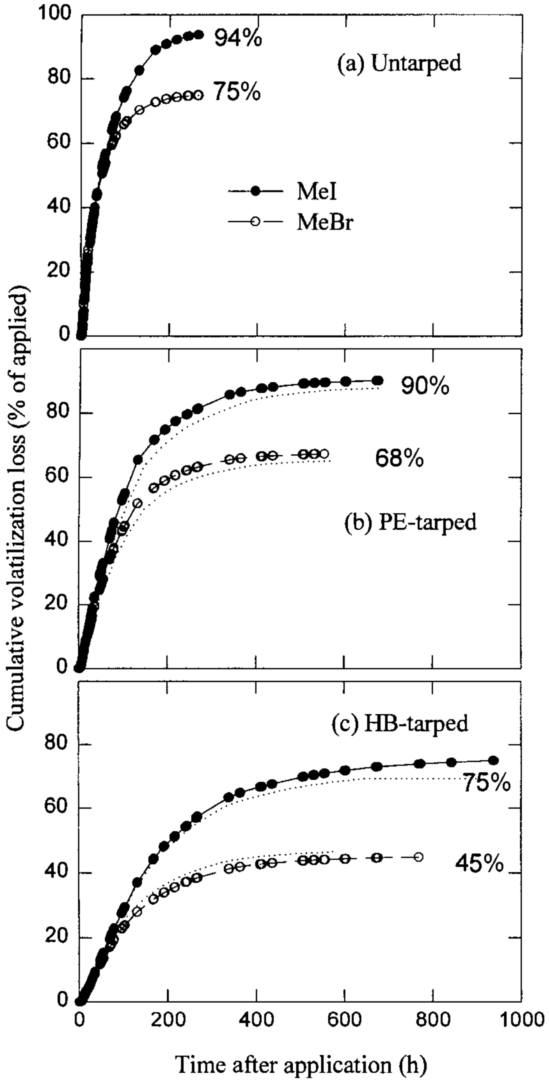

Fig. 2. Cumulative volatilization loss of methyl iodide and methyl bromide from a Greenfield sandy loam in 60-cm packed soil columns when soil surface was (*a*) nontarped; (*b*) tarped with 0.03-mm polyethylene film; and (*c*) tarped with Hyti-bar film. Application of both chemicals was at the 30-cm depth. Dotted lines show data from replicated columns.

ments were obtained in replicated treatments (Gan et al., 1996, 1997). Two treatments in the current study, PE-tarped and HB-tarped, were replicated again to ascertain the consistency of column performance, and the cumulative loss curves are shown in dashed lines in Fig. 2. Since the same amounts of MeI and MeBr were applied under the same conditions, fluxes and losses between these two chemicals in the same treatment should be directly comparable.

In the nontarped column, volatilization of MeBr from the soil surface occurred immediately after the application (Fig. 1a). The maximum flux of MeBr (4.3 mg h^{-1}) was reached at 4.5 to 5 h (see insert in Fig. 1a). MeI volatilization was detected at 1.5 h, and its maximum fluxes were attained at 6 to 10 h, at a level similar to that of MeBr (Fig. 1a). After the peak was reached, volatilization fluxes of both chemicals decreased rapidly. The overall volatilization loss was 75% for MeBr, and 94% for MeI (Fig. 2a). After extrapolation to infinite lower boundary conditions, the total volatilization loss in the nontarped treatment would be 62% for MeBr, and 78% for MeI. In a field study, emissions of MeBr from a nontarped field was 89% within the first 5 d after a shallow (25–30 cm) application (Majewski et al., 1995). Openings caused by injection chisels in the field may have facilitated MeBr loss into the air. As found in this study, even though MeI has a higher boiling point and a lower vapor pressure than MeBr, nontarped applications will still likely result in significant MeI emission losses. Although volatilized MeI is considered to be harmless to the stratospheric ozone, high levels of MeI in the air may be hazardous to workers or nearby residents due to its acute toxicity. Nontarped applications of MeI at shallow depths should therefore be avoided.

When the soil surface was covered with the polyethylene film, the maximum fluxes (1.9–2.1 mg h^{-1}) of MeI and MeBr occurring at 10 to 12 h were only about a half of those from the nontarped column (Fig. 1b). MeBr volatilization was first detected at 1 h, while MeI volatilization was first detected at 2.5 h (Fig. 1b insert). The decline of volatilization fluxes of both MeI and MeBr was more gradual, and detectable volatilization continued for a longer time (670 h or 28 d), than in the nontarped treatment (Fig. 1a and 1b). The total volatilization loss for the tarped treatment was 68% for MeBr, and 90% for MeI (Fig. 2b). After correction for the lower boundary effect, it was estimated that 48% of the applied MeBr, and 72% of the applied MeI, would be emitted for the polyethylene film-tarped treatment. Polyethylene films are commonly used in MeBr fumigation, especially for shallow applications (The United Nations Environment Programme, 1995). A few studies indicate that polyethylene plastics are relatively permeable to MeBr, resulting in insufficient containment or excessive volatilization losses (De Heer et al., 1983; Rolston and Glauz, 1982; Yagi et al., 1993, 1995; Jin and Jury, 1995; Majewski et al., 1995; Yates et al., 1996a,b). This study indicates that polyethylene was even less effective in stopping MeI volatilization loss. This ineffectiveness was partly due to the slower degradation of MeI than MeBr, which left more MeI for volatilization (Gan and Yates, 1996). Though polyethylene tarping did not significantly reduce the overall volatilization loss of MeI, maximum volatilization fluxes were reduced, which may be beneficial for minimizing worker or residential exposure.

When the surface cover was the less permeable Hyti-bar film, MeI or MeBr volatilization further decreased (Fig. 1c). The maximum fluxes, at 0.7 to 0.76 mg h^{-1} for both chemicals, were only ≈15% of that from the nontarped column, and 40% of that from the PE-tarped column. Methyl bromide and MeI were first detected at 1.5 and 3.0 h, respectively (Fig. 1c). Measurable volatilization of MeI continued for 940 h, or 39 d. The total cumulative volatilization loss was 45% for MeBr and 75% for MeI (Fig. 2c). After correction for lower boundary effect, the volatilization loss was extrapolated to be 27% for MeBr, and 52% for MeI. The Hyti-bar film apparently served as a better barrier than polyethylene film in keeping MeI or MeBr in the soil, and less volatilization loss occurred as a result of more extensive degradation. The use of a less permeable plastic Saranex in the Netherlands resulted in drastic reduction in MeBr emissions, and significant increase in soil Br^- (Hamaker et al., 1983; Wegman et al., 1983).

In all the treatments, the time that volatilization flux of MeI became measurable was 1.5 h later than for MeBr. The delay in MeI volatilization during the initial hours may be beneficial in providing a time window for better worker protection. It may also allow additional procedures, such as packing the surface to close chisel openings, or surface irrigation (Jin and Jury, 1995), to be incorporated into the fumigation process to further reduce volatilization. The delay in MeI volatilization may be attributed to its higher boiling point (42°C vs. 4°C for MeBr) and lower vapor pressure (400 vs. 1600 mm Hg for MeBr). The time needed for liquid fumigant to vaporize can be estimated from the equation derived by Bird et al. (1960):

$$V = SF_s\sqrt{(4D_e t/\pi)} \qquad [1]$$

where V is volume of vapor a fumigant forms [m^3 (gas)]; S is surface area of vaporization (m^2); F_s is the saturated vapor pressure of a fumigant divided by the total pressure; and t is time (s). Assuming applied MeI and MeBr are exposed to the same conditions, the time for the same molar amount of MeI to completely vaporize is roughly 20 times that for MeBr.

Volatilization from Different Soils

When the soil surface was covered with polyethylene film, volatilization of MeBr and MeI varied greatly depending on the type of soil in the columns (Fig. 3, 4, 1b, and 2b). While the maximum fluxes were similar in columns packed with Greenfield SL (Fig. 1b), Carsitas LS (Fig. 3a) and Linne CL (Fig. 3b), volatilization of both MeI and MeBr in the later two soils decreased more rapidly after maximum fluxes were reached; and detectable volatilization stopped much sooner than in the Greenfield soil. The maximum volatilization fluxes from the potting mix column (Fig. 3c) were smaller than that from the other soil columns, but the total volatilization loss was similar to that from the Carsitas LS. The measured or extrapolated cumulative volatilization losses for both chemicals follow the order: Greenfield SL > Linne CL > Carsitas SL ≈ potting mix (Table 2).

The diffusion of a volatile compound such as a fumigant in fairly dry soil that is typical of fumigation is predominantly through the vapor phase (Jury et al., 1983; Jin and Jury, 1995). Therefore diffusion in the water phase and advection may be ignored and fumigant transport may be simplified as below for the experimental conditions:

$$\frac{\partial C_g}{\partial t} = D_s\frac{\partial^2 C_g}{\partial z^2} - \mu C_g \qquad [2]$$

$$\frac{\partial C_g}{\partial t}\bigg|_\infty = \text{infinite} \qquad [3]$$

$$C_g(z,0) = f(z) \qquad [4]$$

$$D_s\frac{\partial C_g}{\partial z} = h[C_g - C_{air}] \qquad [5]$$

where C_g is fumigant concentration in soil vapor phase (mg cm^{-3}); t is time (d); D_s is effective diffusion coefficient of fumigant in soil gas phase ($cm^2\ d^{-1}$); z is distance (m); μ is degradation rate constant of fumigant in soil (d^{-1}); C_{air} is fumigant concentration in the atmosphere (mg cm^{-3}); and h is the mass transfer coefficient (cm d^{-1}). From the model, it is apparent that soil diffusion and volatilization of a fumigant are affected by its diffusion coefficient, degradation or persistence in soil, and the resistance (i.e., $1/h$) to vapor transport between the soil and atmosphere. In extrapolating measured column volatilization fluxes, D_s for different soil columns was calculated (Table 1). Different packing conditions (i.e., water content and bulk density) and adsorption coefficients (Gan and Yates, 1996) resulted in large D_s for the Linne CL column. The higher emission loss of MeBr and MeI from the Linne CL compared with the Carsitas LS and potting mix could be partially attributed to the difference in their D_s values. However, the substantial difference in volatilization losses between these three columns and the Greenfield SL column was clearly due to a different term—*degradation*. The half-degradation

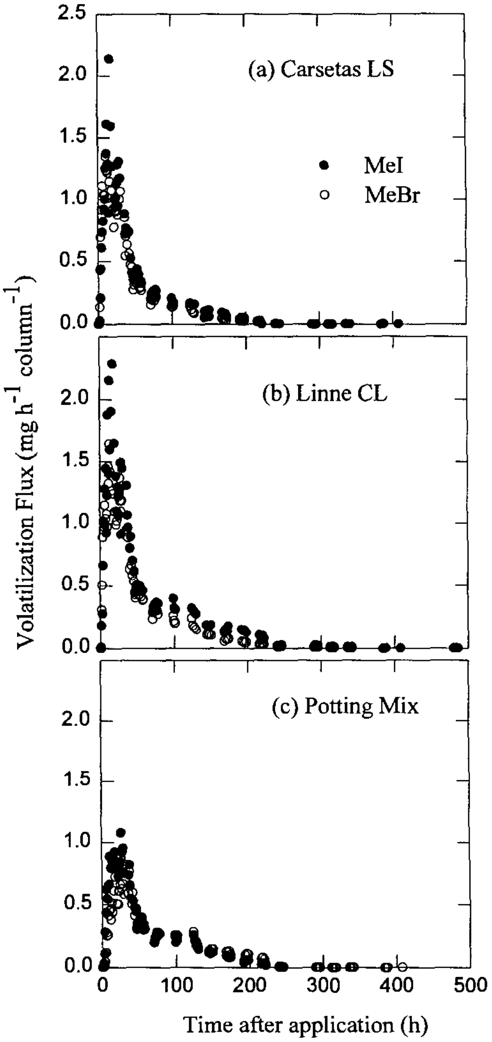

Fig. 3. Volatilization fluxes of methyl iodide and methyl bromide from 60-cm columns packed with different soils under 0.03-mm polyethylene film-tarped conditions. (*a*) Carsitas loamy sand; (*b*) Linne clay loam; and (*c*) a nursery potting mix. Application of both chemicals was at the 30-cm depth.

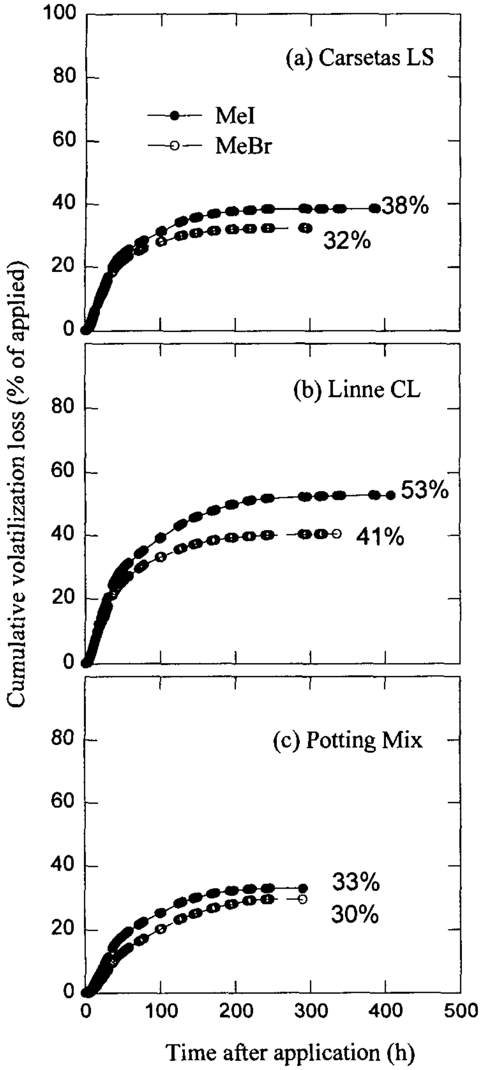

Fig. 4. Cumulative volatilization loss of methyl iodide and methyl bromide from 60-cm columns packed with different soils under 0.03-mm polyethylene film-tarped conditions. (*a*) Carsitas loamy sand; (*b*) Linne clay loam; and (*c*) a nursery potting mix. Application of both chemicals was at the 30-cm depth.

time ($t_{1/2}$) for MeI degradation was estimated to be 17 d for the Greenfield SL, but only 4, 5, and 5 d for the Carsitas LS, Linne CL and the potting mix, respectively; while the $t_{1/2}$ for MeBr was 9 d for the Greenfield SL, but only ≈2 d for the other three matrices (Gan and Yates, 1996). According to Eq. [2], degradation depletes the fraction of fumigant that is available for volatilization in the soil, thus decreasing volatilization losses.

Distribution in Soil

Column Experiments

Measured (in symbols) and model fitted (in lines) fumigant concentrations in soil air are given in Fig. 5 for the Greenfield SL under various surface conditions and in Fig. 6 for different soils under polyethylene tarped conditions. Fitted data generally agreed well with the measured points. In the packed soil columns, due to the closed column bottom, fumigant distribution was distorted a few hours after the application due to the build up of concentrations at 60 cm. Under the same conditions, MeI behaved to a great extent like MeBr (Fig. 5 and 6). However, in the same soil column, especially during the initial hours, MeBr consistently spread out more rapidly than MeI. This difference was likely due to their different boiling points and diffusion rates. The estimated D_s for MeBr was consistently greater than that for MeI under the same conditions (Table 1).

Table 2. Measured and extrapolated total volatilization losses of methyl iodide (MeI) and methyl bromide (MeBr) after application at 30 cm in soil (% of applied chemical).†

Treatment	MeI		MeBr	
	Measured	Extrapolated	Measured	Extrapolated
Greenfield SL-nontarped	94	78	75	62
Greenfield SL-PE-tarped	90	72	68	48
Greenfield SL-HB-tarped	75	52	45	27
Carsitas LS-PE-tarped	38	31	32	26
Linne CL-PE-tarped	53	42	41	30
Potting Mix-PE-tarped	33	28	30	24

† Extrapolation of measured volatilization losses to the infinite lower boundary condition was performed by fitting soil gas concentrations to a vapor transport model.

In the nontarped column, MeI or MeBr concentrations at the soil surface (at 0–10 cm depth in Fig. 5a) were very low, indicating that in the field, nontarped fumigation will unlikely provide adequate control of the pests dwelling near soil surface (e.g., weeds). Covering the soil surface with plastic films clearly increased fumigant concentrations near the soil surface (Fig. 5b and 5c), and the overall fumigant concentrations were higher than in the nontarped column throughout the experiment. In polyethylene film-tarped field plots, MeBr concentrations at various depths were greater than in nontarped ones (Abdalla et al., 1974). Even though polyethylene film was relatively ineffective in reducing MeI volatilization, it nevertheless acted as a short-term barrier. Increased MeI concentrations in tarped soil indicate that tarped MeI fumigation should be more effective than nontarped fumigation.

The vertical distribution of MeI and MeBr was also determined in columns packed with different soils (Fig. 6; data for Greenfield SL are in Fig. 5b). Soil type clearly had an effect on MeI or MeBr distribution in the soil. This soil dependence is probably caused by the different soil water contents and bulk densities of the columns, and different degradation rate constants and adsorption coefficients in these soils. In the Carsitas LS, Linne CL and the potting mix (Fig. 6), MeI and MeBr concentrations in the soil became substantially smaller with time than that in the Greenfield SL (Fig. 5b). Degradation might have partly contributed to the observed rapid fumigant depletion from these soils. From the perspective of efficacy, the same dosage of MeI or MeBr in an organic matter-rich soil might not produce the same control as in an organic matter-poor soil.

Field-Plot Experiments

The movement of MeI and MeBr was measured in the field, where a restrictive lower boundary as in the

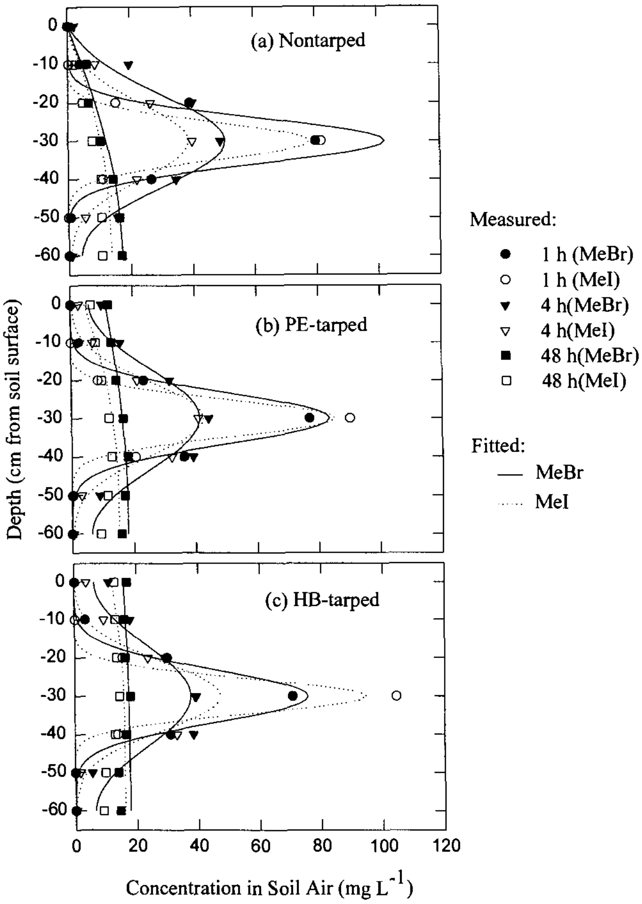

Fig. 5. Measured (symbols) and fitted (lines) fumigant concentrations in soil air at different depths in 60-cm columns packed with Greenfield sandy loam under various surface conditions. (*a*) nontarped; (*b*) 0.03-mm polyethylene film-tarped; and (*c*) Hyti-bar film-tarped. Application of both chemicals was at the 30-cm depth.

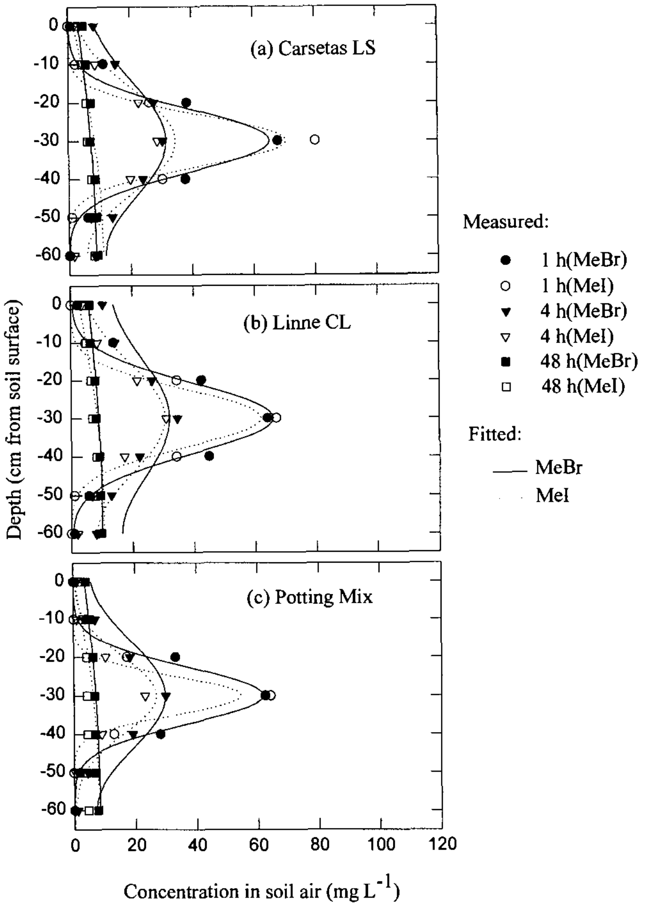

Fig. 6. Measured (symbols) and fitted (lines) fumigant concentrations in soil air at different depths in 60-cm columns packed with different soils under 0.03-mm polyethylene film-tarped conditions. (*a*) Carsitas LS; (*b*) Linne CL; and (*c*) a nursery potting mix. Application of both chemicals was at the 30-cm depth.

column system was not present (Fig. 7). Since the sampling probe was installed very close (within 15 cm) to the source, the data should reflect the vertical movement of the fumigant. Also, because a large amount of chemical was applied as a point source, the downward movement of fumigants in this particular case might reflect a worst-case scenario.

The distribution of MeI and MeBr in soil can be described in three phases. During the first phase that extended for the first few hours after application, MeBr diffused rapidly from the application point (30 cm below the surface) in all directions. In contrast, diffusion of MeI was more limited, and after 1 h, only a small portion had reached the sampling point (Fig. 7a). The slower diffusion of MeI was in agreement with the delay in detectable volatilization as well as the slower diffusion observed with packed columns. During the second phase lasting from a few hours to a few days, concentrations of both MeBr and MeI around the injection depth decreased very rapidly with time, and became very small 72 h after application (note the different x-axis scales in Fig. 7). Concentrations of MeI quickly approached and then surpassed those of MeBr around the depth of placement (Fig. 7b–7d). Methyl iodide was more confined to the layers adjacent to the depth of placement than MeBr. This was likely caused by its slower diffusion, which is in agreement with the difference in D_s for MeBr and MeI in packed soil columns (Table 1). The polyethylene plastic barrier was apparently not effective in stopping volatilization, since MeI and MeBr in the top soil layers were quickly depleted, which caused the center of mass to appear to be moving downward (Fig. 7). In the third phase (after 120 h), concentrations of MeI became higher than MeBr at most depths (Fig. 7e and 7f). For instance, 10 d (240 h) after application, the concentration of MeI at 180 cm was more than three times that of MeBr (Fig. 7f). The fact that MeI remained in soil at higher levels at the later stage was likely because of its longer persistence than MeBr under the same conditions (Gan and Yates, 1996). The higher residual concentrations of MeI in soil imply that should MeI and MeBr have similar biological activities, the same dosage of MeI may provide better control than MeBr. On the other hand, the increased likelihood for MeI over MeBr to contaminate groundwater will depend on the soil and surface conditions. If the soil is slow in degrading MeI and its surface is covered, as in this field study, a small fraction of the applied chemical may reach groundwater if the water table is shallow. However, because of its high volatility, MeI in water dissipates rapidly through volatilization once the water is exposed to the air (Gan and Yates, 1996). Additional studies on the fate and toxicological effects of MeI in water should be conducted.

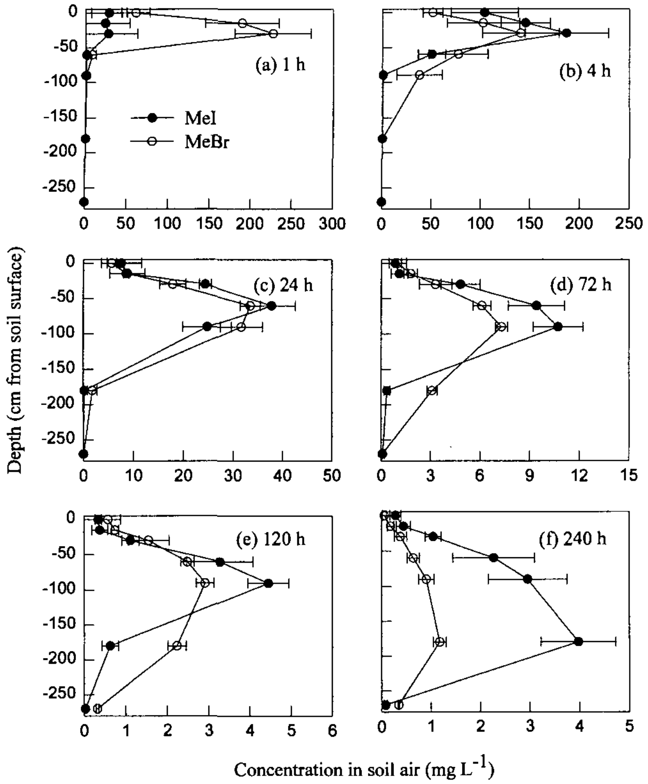

Fig. 7. Fumigant concentrations in soil air measured at different depths in field plots after a point-source application at 30 cm under 0.1-mm polyethylene film-tarped application. Time after application: (*a*) 1 h; (*b*) 4 h; (*c*) 24 h; (*d*) 72 h; (*e*) 120 h; and (*f*) 240 h.

CONCLUSIONS

MeI behaved, to a great extent, like MeBr after subsurface application as would be expected from their similarities in structure and physical-chemical properties. This could be advantageous in that application techniques and management practices that are in use for MeBr may be directly adopted for MeI. A few differences, however, between MeI and MeBr were noticed in their volatilization into the air and distribution in soil. Loss of MeI through volatilization after subsoil application was found to be even greater than MeBr. The commonly used polyethylene film was ineffective in reducing the overall volatilization loss of MeI, but it reduced the maximum volatilization fluxes and increased MeI concentrations in surface soil layers. Greater MeI volatilization losses were likely caused by its slower degradation in soil than MeBr. Volatilization losses of both MeI and MeBr varied in different soils, and were significantly reduced in organic matter-rich soils which were capable of more rapidly degrading the chemicals. After subsurface application, MeI volatilization from the soil surface was temporarily delayed because of its lower vapor pressure, which may reduce worker exposure to MeI vapor during fumigation. Methyl iodide distribution in soil was more confined to the layers adjacent to the application point, and concentrations of MeI remained higher for a longer period of time. If the two chemicals have similar biological activity and the infested zones are close to the point of application, MeI will likely provide a better control than MeBr. In fields where water table is shallow, it is possible that MeI may reach the groundwater owing to its longer persistence. The potential for MeI to cause groundwater contamination needs further study under different application and soil regimes.

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