Research

Effect of Application Variables on Emissions and Distribution of Fumigants Applied via Subsurface Drip Irrigation

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Soil fumigation is useful for controlling soil-borne pests and diseases in high-cash-value crops. Fumigants are highly volatile, and approaches to reduce atmospheric emissions are required to protect human and environmental health. Application of fumigants through drip irrigation has been proposed as a means to decrease fumigant emissions, improve fumigant distribution in soil, and minimize worker exposure. These experiments were conducted to investigate the effect of the configuration of the drip system on the volatilization and distribution of the fumigants 1,3-dichloropropene (1,3-D), propargyl bromide (PrBr), and methyl isothiocyanate (MITC) in bedded systems. Results indicated that changing the drip emitter spacing and using multiple drip lines in each bed had little effect on the emissions and distribution of any fumigant. Increasing the depth of application from 15 to 30 cm reduced volatilization of MITC by ~20 to >90%; emissions were reduced due to a decrease in the flux from the bed top, and deeper injection did not change the amount of fumigant volatilized from the bed side slope and furrow. Increasing the application depth resulted in a slight decrease in the rate of fumigant dissipation in soil, indicating the potential for some improvement in pest-control efficacy with deeper application.

Introduction

Soil fumigation is an important component of intensive agriculture, primarily used for the control of nematodes, weeds, insects, and soil-borne diseases in fruit and vegetable production. Methyl bromide is a highly effective soil fumigant that is being phased out in the United States and other developed countries according to the Montreal Protocol. Alternative fumigants that are currently commercially available include 1,3-dichloropropene (1,3-D), chloropicrin (CP), and methyl isothiocyanate (MITC). Other efficacious chemicals, including iodomethane and propargyl bromide (PrBr),

are being investigated for their potential to serve as soil fumigants. Because fumigants have relatively high vapor pressures, low boiling points, and high air–water partitioning coefficients, they are highly mobile in the gas phase and a large fraction of the applied chemical may be lost via volatilization from the soil surface following application. Fumigants are also air toxic compounds and their concentration in air surrounding fumigated fields is the basis for many regulations restricting their use. There is interest in developing economically feasible management practices that reduce fumigant emissions while maintaining efficacy and productivity.

Approaches that increase the residence time of fumigants in soil decrease emissions by increasing the proportion of fumigant that is transformed in soil before it can be lost to the atmosphere. These approaches include increasing the soil water content, increasing the depth of application, and increasing the soil bulk density. Increasing the soil moisture decreases the overall rate of fumigant diffusion in soil by restricting gas-phase diffusion. Increasing the soil water content may affect pest-control efficacy due to changes in fumigant phase partitioning, transformation, and availability (*1, 2*). In a series of controlled laboratory experiments, Gan et al. (*3*) demonstrated that increasing the (initially uniform) soil water content decreased the maximum and cumulative emissions of methyl bromide. The decrease in emissions was accompanied by an increase in total fumigant remaining in the soil, indicating that the decrease in emissions was due to a decrease in diffusion rather than an increase in transformation rate.

Increasing the bulk density of the soil decreases emissions by decreasing the air-filled porosity of the soil, restricting gas-phase diffusion. Soil fumigation often includes compaction of the soil surface. In laboratory columns, increasing the soil bulk density from 1.40 to 1.70 g cm^{-3} reduced cumulative emissions of methyl bromide from 77 to 53% of the applied mass (*3*). Increasing the depth of application increases the path length from the point of injection to the soil surface, resulting in an increase in soil residence time that can decrease emissions. The extent of emissions reduction achieved by increasing soil residence time depends on the rate of degradation of the fumigant in the soil (*4*). Soils that rapidly degrade the applied fumigant (typically soils with high organic matter content or soils that contain a soil microbial community capable of rapidly degrading the fumigant) demonstrate a stronger impact of these management practices.

Application of fumigants through drip irrigation systems (*5*) has been proposed as a means to decrease fumigant volatilization, because the addition of water decreases gas-phase diffusion. Little information exists regarding the volatilization of fumigant compounds following subsurface drip application. Laboratory experiments (*6*) indicated that when 1,3-D was applied with water at 20-cm depth (simulating subsurface drip application), cumulative emissions of 1,3-D from bare soil were ~20% of the applied mass, a decrease of approximately 2.5 times compared to simulated shank injection to untarped soil at 20-cm depth. However, surface drip application to untarped soil resulted in rapid flux from the soil surface and high cumulative emissions: >90% of the applied mass was lost via volatilization when 1,3-D was applied by surface drip (*6*). Other laboratory studies simulating drip application of 1,3-D at 10-cm depth indicated cumulative emissions of ~45–50% of the applied mass (*7*).

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Similar results were observed in a field experiment in which 1,3-D was applied by subsurface drip at 10-cm depth (8), where 32% of the applied 1,3-D was lost through volatilization from bare soil. The results of these investigations suggest that application of fumigants by drip irrigation will be most effective in reducing emissions if the fumigant is applied at sufficient depths to prevent rapid volatilization from the soil surface.

Difficulties in achieving a uniform distribution of MITC following soil application of metam sodium can lead to poor pest control efficacy (9). Metam sodium is most often applied to soil with water, either by sprinkler or drip irrigation. Fumigant application through drip irrigation may be useful for increasing the uniformity of fumigant distribution in soil and is expected to increase in popularity (5). Since field preparation and installation of plastic tarp are conducted prior to fumigant application, this application procedure decreases the number of workers in the field during the fumigant application, thus enhancing worker safety.

Fumigant emissions following application through drip irrigation systems has not been well-addressed. The objectives of these experiments were to systematically investigate the impact of the configuration of the drip irrigation system on the volatilization and soil distribution of existing (1,3-D isomers and MITC) and proposed (PrBr) fumigants following subsurface drip application to soil beds. The factors investigated included the depth of application, spacing of emitters on the drip line, and the number of drip lines in each bed. The effect of application depth on emissions of 1,3-D and MITC following subsurface drip application was further investigated in a field study conducted in sandy loam soil. Flux was measured from all portions of the bed (top, side slope, and furrow) to indicate the total flux occurring from these bedded systems.

Materials and Methods

Commercial formulations of fumigants were obtained from the manufacturers. Samples of Telone C-35 (61% 1,3-D and 35% CP) and InLine (an emulsifiable concentrate of 1,3-D containing 61% 1,3-D and 33.3% CP) were provided by Dow AgroSciences (Indianapolis, IN). Vapam (42% sodium methyldithiocarbamate), an MITC precursor, was donated by Amvac Chemical Corp. (Los Angeles, CA). Propargyl bromide (80% in toluene) was provided by Albemarle Corp. (Baton Rouge, LA). InLine and Vapam are formulations labeled for application by subsurface drip. Propargyl bromide is an experimental product not registered for use as a soil fumigant. Analytical standards of 1,3-D and MITC were purchased from ChemService (West Chester, PA). A sample of HDPE with a nominal thickness of 1.5 mil (0.038 mm), which is typical of that currently used in soil fumigation, was obtained from TriCal, a commercial fumigant applicator.

Sand Mesocosm Experiments. Two experiments were conducted in concrete mesocosms (3 m long × 1.5 m wide × 1.6 m deep, Figure 1A) located at the George E. Brown Jr. Salinity Laboratory in Riverside, CA. Mesocosms are filled with washed river sand to a bulk density of 1.7 Mg m^{-3}. The sand is coarse-textured, with a computed equivalent mean particle radius of 0.51 mm and an estimated mean void radius of 0.35 mm (10). The first experiment, conducted January 14−28, 2002, included four treatments: (a) depth of drip line, 15 cm; emitter spacing, 15 cm; (b) depth of drip line, 15 cm; emitter spacing, 30 cm; (c) depth of drip line, 30 cm; emitter spacing, 15 cm; and (d) depth of drip line, 30 cm; emitter spacing, 30 cm. Beds were formed at the soil surface, measuring 20 cm high and 50 cm across the top of the bed (Figure 1A). A trench was dug in each bed to a depth of 15 or 30 cm. Drip irrigation tubing (16 mm diameter HDPE) with built-in emitters at 30 cm spacing and a flow rating of 3.8 L h^{-1} was placed in the trench for treatments b and d.
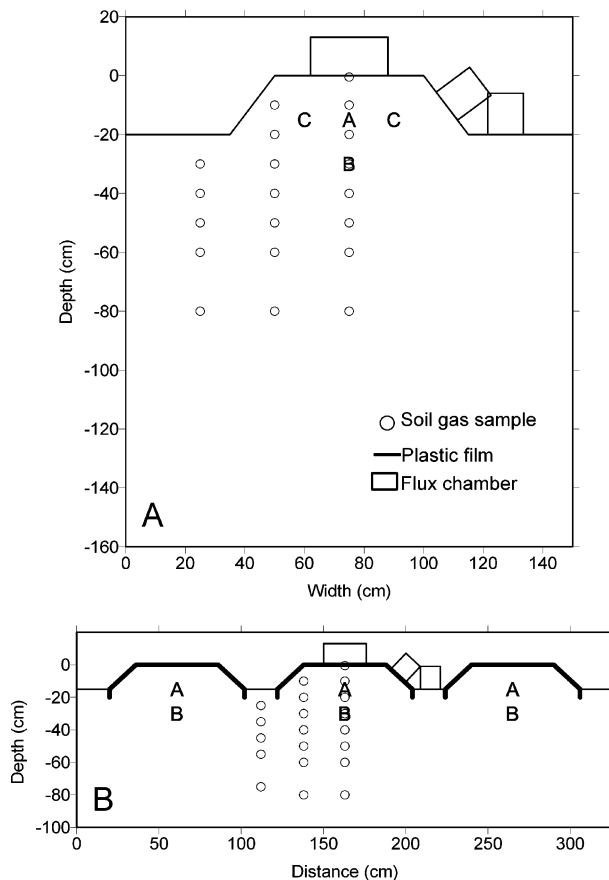

FIGURE 1. Dimensions and locations of beds, passive chambers, and soil gas samples in the (A) sand mesocosm and (B) field experiments. Letters indicate the location of drip irrigation lines in different treatments.

Drip tubing with emitter spacing of 15 cm (treatments a and c) was simulated by installing two drip lines with 30 cm spacing offset by 15 cm in the same trench. The trench was backfilled, the bed reshaped, and the soil surface packed by tapping with a flat board.

The second experiment, conducted March 4−12, 2002, included treatments (a) a single drip line with emitter spacing of 30 cm placed at the center of the bed at 15-cm depth and (b) two drip lines with emitter spacing of 30 cm placed 15 cm from the center of the bed (30 cm spacing between lines) at a depth of 15 cm (Figure 1A). Bed formation and drip line installation were the same as in the first experiment. For both experiments, triplicate mesocosms were used for each treatment, and beds were left untarped. The mesocosms had not been previously treated with fumigants.

Plastic carboys (25 L total volume) were used as source vessels, one for each mesocosm. Water (24 L) was placed in each carboy, followed by PrBr (29 mL), Telone C-35 (44 mL), and Vapam (72 mL). For treatments with two drip lines, fumigant solution was split between two carboys, each containing 12 L of solution, so that the total volume of water applied was the same for all mesocosms. Application rates were field-relevant: 98 L ha^{-1} for Telone C-35, 160 L ha^{-1} for Vapam, and 81 kg ha^{-1} for PrBr. Carboys were sealed and shaken to mix. Application through the drip lines was achieved by connecting the sealed carboys to the drip line using HDPE tubing and pressurizing the carboys to 55 kPa. Fumigation required 2−3 h, and carboys were shaken periodically to maintain a uniform solution concentration.

A weather station was installed on-site to monitor air temperature relative humidity, precipitation, and other climatic variables during each experiment. For the first

experiment, the mean air temperature was 11.0 °C (range from −4 to 24), the mean relative humidity was 43.6% (range from <10 to 93), and 0.56 cm of rain fell on the final day of the experiment. For the second experiment, the mean air temperature was 14.5 °C (range from 6 to 27), the mean relative humidity was 47.0% (range from <10 to 92%), and 0.15 cm of rain fell 60−88 h after fumigant application.

Field Experiment. Emissions under field conditions were investigated at the University of California Agricultural Experiment Station in Riverside. The field site is within a few kilometers of the mesocosm site. The soil was an Arlington sandy loam (coarse-loamy, mixed, thermic, Haplic Durixeralf) comprised of 75% sand, 18% silt, and 7% clay; the soil contains 9.2 g kg^{-1} organic carbon and the pH is 6.7. Compared to the sand in the mesocosms, the field soil is finer textured and less uniform. The computed mean particle radius of the field soil is 0.12 mm (>4 times smaller than the mesocosm sand) and the estimated mean void radius is 0.03 mm (>10 times smaller than the mesocosm sand) (*10*). The field experiment was conducted on December 9−16, 2002. A weather station installed at the site indicated a mean air temperature of 11.6 °C (range from 2 to 22) and a mean relative humidity of 70% (range from 20 to 97); there was no measurable precipitation during the flux experiment.

Beds were formed, measuring 15 cm high, 50 cm across the top with 20 cm furrows (Figure 1B). Drip line (16 mm polyethylene with 3.8 L h^{-1} emitters spaced 30 cm apart) was mechanically installed in each bed at nominal depths of 15 and 30 cm. Beds were mechanically tarped with HDPE (Figure 1B). Duplicate rows 10 m in length were used for each treatment, and beds were arranged in a completely randomized design. The mean hourly averaged soil temperature was 12.9 °C (range from 1.2 to 34.2) directly under the HDPE tarp, 13.8 °C (range from 6.4 to 24.4) at 2.5-cm depth, 13.6 °C (range from 7.7 to 21.6) at 5-cm depth, 13.7 °C (range from 9.7 to 18.4) at 10-cm depth, 13.8 °C (range from 11.4 to 16.5) at 20-cm depth, 14.1 °C (range from 13.0 to 15.4) at 30-cm depth, 14.5 °C (range from 14.0 to 15.2) at 40-cm depth, and 14.8 °C (range from 14.4 to 15.3) at 50-cm depth. Mean bare soil temperatures were 0.6 °C (at 30−40-cm depth) to 1.8 °C (at 2.5-cm depth) lower than tarped soil temperatures.

Fumigants were added at the same rate as in the sand mesocosm experiments, but because of a lack of available material, PrBr was not included in the field experiment. Measured amounts of fumigants (3.6 L of InLine and 5.9 L of Vapam) were added to 190 L of water in a closed commercial polyethylene mixing tank and continuously stirred by a stainless steel impeller. The fumigant and water mixture was injected into the irrigation water by a positive displacement chemigation pump (Injecto-O-Meter Manufacturing Co., Clovis, NM). Solution was passed through brass flow meters and a pressure regulator set at 11 psi. The fumigant solution was transported 200 m through buried 2.5-cm diameter PVC pipe to the beds in the field. At the field, each stream was split into 15 drip lines by a buried manifold. These experiments used 12 of the 30 treated rows. Fumigant application required ∼3 h, and application rates were 98 L ha^{-1} for InLine and 160 L ha^{-1} for Vapam. Following fumigant application, an additional 340 L of freshwater were added to the drip irrigation system to rinse the lines.

Monitoring Emissions. Volatilization was measured using open-bottomed metal passive chambers that were placed on the center of the bed top, the side slope of the bed, and in the furrow adjacent to the side slope (Figure 1). In the field study, flux was monitored on the center row of three rows with the same application conditions, the outside rows acting as buffers between treatments (Figure 1B). Chambers were placed on the soil surface for 30 min. Syringes were used to collect samples (100 mL) from each passive chamber following the 30-min interval. An adsorbent tube (activated

charcoal for the sand mesocosm study, XAD-2 for the field experiment) was placed between the chamber and the syringe to extract the fumigants from the air stream. Following sample collection, adsorbent tubes were capped on both ends and transported to the laboratory, where they were frozen at −21 °C until extraction. Chambers were removed and aerated between sampling times. Adsorbent was extracted using 3 mL of acetone. Calibration standards were spiked to adsorbent tubes and extracted using the same method. An aliquot of the solvent extract was transferred to a GC vial for analysis by GC, using a microelectron capture detector (for 1,3-D and PrBr) or nitrogen−phosphorus detector (for MITC). Recoveries of all monitored fumigants in laboratory-spiked samples (fumigants in liquid phase) were 95−101% for both adsorbents. Preliminary experiments indicated that fumigant concentrations did not change during storage at −21 °C.

Volatilization fluxes (μg m^{-2} s^{-1}) were determined using

$$\text{flux} = X_t V_c / A V_s T_s$$

where X_t is the amount of fumigant in the adsorbent tube (μg), V_s is the volume of gas removed from the chamber (100 mL), V_c is the chamber volume (mL), A is the chamber base surface area (m²), and T_s is the chamber placement time (30 min or 1800 s). Fluxes were calculated for each bed dimension (top, side slope, and furrow) and summed to provide a measurement of the total flux at each measurement time. Flux was monitored at 45 time points spanning 346 h in the first sand mesocosm experiment, 38 time points spanning 194 h in the second sand mesocosm experiment, and 32 time points spanning 170 h in the field experiment. Sampling times are indicated by the data points in Figure 2. Flux was integrated over time to give an estimate of the total volatilization (as a percentage of the applied mass). Complete conversion of Vapam to MITC was assumed in calculations of MITC volatilization. Nearly complete (90−98%) conversion of metam sodium to MITC has been observed within 1 d after application in a variety of soils (*11*).

Monitoring Fumigant Distribution. In the first sand mesocosm experiment, the distribution of fumigants in the soil air of the root zone was measured at 2, 3, 4, 7, and 8 d after application using push probes. Probes were constructed of 6.4 mm o.d. stainless steel tubing 1.0 m in length that was capped on one end. Stainless steel tubing (1.6 mm o.d.) was placed inside this tube for sample delivery. The outer tubing was slotted for the lower ∼1 cm to allow entry of the air sample; glass wool was loosely packed in the slotted portion to provide a particulate filter. The inner tubing ran the length of the sampler from the slotted area to the top of the outer tube. For sample collection, Teflon tubing was connected to the inner stainless steel tubing, and a charcoal adsorbent tube was fitted to the opposite end of the Teflon tubing using a short length of latex tubing. A gas sample (50 mL) was drawn through the adsorbent tube using a syringe to apply vacuum and measure the sample volume. In the second sand mesocosm experiment, gas samples were collected 1, 2, 3, 4, 7, and 8 d after fumigant application from buried Teflon tubes as described in Papiernik et al. (*12*). In both sand mesocosm experiments, gas samples were collected at the center of the bed, the edge of the bed, and in the furrow, as indicated in Figure 1A. Adsorbent tubes were extracted and analyzed as described for the flux samples. Concentration data were kriged to construct contour maps of soil gas concentrations throughout the soil profile. The volume contained under the contours was determined to estimate the mass of fumigant remaining in the monitored zone of each bed at each sampling time.

Statistical Analyses. Calculated results for the cumulative emissions, maximum flux, time to maximum flux, flux occurring in the first 40 h after application, and flux from the
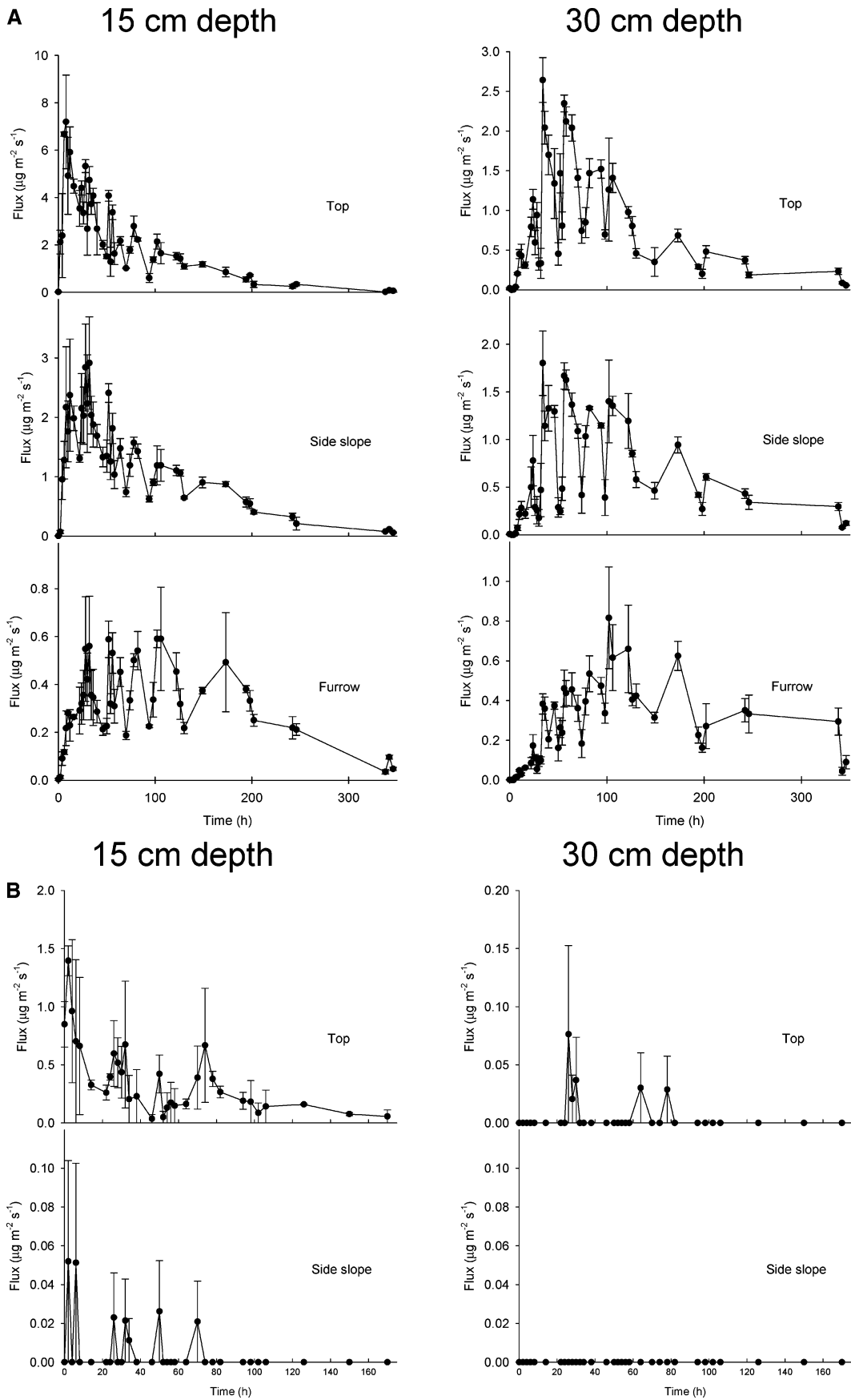
FIGURE 2. Methyl isothiocyanate (MITC) flux in the (A) first sand mesocosm experiment and (B) field experiment. Emitter spacing was 30 cm. Values indicate the mean of triplicate mesocosms or duplicate rows (for the field experiment). Error bars indicate the standard error. Flux from the furrow was negligible in the field experiment.

bed top, side slope, and furrow were subjected to statistical analyses. Each experiment was set up as a one-way ANOVA model, with treatment as the fixed effect factor. For the first sand mesocosm experiment, the treatments included combinations of emitter spacing and application depth. For the second mesocosm experiment, treatments included application via a single drip line or two lines spaced 30 cm apart. For the field experiment, treatments included application at 15- and 30-cm depth.

For each experiment, multiple fumigant compounds (cis-1,3-D, trans-1,3-D, MITC, and PrBr) were measured on each response variable; therefore, the response data was analyzed using a one-way multivariate analysis of variance (MANOVA) model. The field experiment data was right-skewed, had heterogeneous variance, and contained 0 values; therefore, the specific log transformation $Z = \ln(X + 1)$ was used, where X is the appropriate dependent variable. This transformation corrected the nonconstant variance problem and helped induce approximate residual normality, facilitating valid test statistics. Residual diagnostics confirmed that the one-way MANOVA models were appropriate, that the residual normality assumptions appeared reasonable, and that the residual errors across the four fumigants were highly correlated.

Both multivariate and univariate testing procedures were used, with all procedures designed to protect the overall experimental error rate ($\alpha = 0.05$). The difference between treatments was tested by first performing a MANOVA test for treatment differences across all four fumigants simultaneously (13). If this test was found to be statistically significant ($p < 0.05$), then univariate ANOVA models were fit to each fumigant individually, and Tukey's mean separation tests were used to determine statistically significant treatment differences at the 0.05 level (14).

To analyze the differences in volatilization between fumigants, the average responses across fumigants were tested for equivalence using a second MANOVA test. If this second test was found to be statistically significant, then individual pairwise fumigant contrast tests were performed. To preserve an overall 0.05 experimental error rate, a Bonferroni adjusted significance level was used to test for the statistical significance of these individual pairwise contrasts (13). All fumigant means associated with pairwise contrasts having p-values below the Bonferroni-adjusted value were judged to be significantly different at the 0.05 level.

Results and Discussion

Fumigant Emissions. Sand mesocosm experiments were conducted to indicate the potential for application parameters to affect fumigant emissions under ambient weather conditions in a relatively homogeneous, unreactive soil. The field experiment indicated the effect of application depth on fumigant emissions in a natural soil. In the first sand mesocosm study, ~26% of the applied 1,3-D and PrBr and 17% of the applied MITC were lost via volatilization (Table 1). These emissions rates are similar to those observed in laboratory and field studies, which indicated volatilization losses of 20% (6) to 32% (8) for 1,3-D applied to bare soil by subsurface drip irrigation. Volatilization losses of 17−34% have been reported for MITC applied at 10−20-cm depth with no water addition (15, 16). Cumulative volatilization rates were lower in the field experiment, probably due to the low air temperatures, high relative humidity, use of a surface tarp (HDPE), and more rapid fumigant transformation in the field soil compared to the sand mesocosms.

In all experiments, cumulative emissions of PrBr were similar to that of the 1,3-D isomers, while volatilization of MITC was significantly lower than that of the other fumigant compounds (Table 1). This trend follows that of the air−water partitioning coefficient (K_H) at 20 °C, which is 0.01 for MITC, 0.041 for trans-1,3-D, 0.056 for cis-1,3-D (4), and 0.037

TABLE 1. Cumulative Emissions (% of applied) of Fumigants from Soil under Different Application Conditions[a]

treatment depth (cm)	emitter spacing (cm)	lines	cis-1,3-D	trans-1,3-D	MITC	propargyl bromide
Sand Mesocosm Experiment 1 (Bare Soil Surface)						
15	30	1	32.2 a	31.6 a	21.5 a	27.9 a
15	15	1	24.4 a,b	24.7 a,b	18.8 a,b	25.8 a
30	30	1	26.9 a,b	25.5 a,b	13.4 c	24.5 a
30	15	1	22.9 b	22.5 b	15.6 b,c	25.0 a
Sand Mesocosm Experiment 2 (Bare Soil Surface)						
15	30	1	13.2 a	12.7 a	5.5 a	9.7 a
15	30	2	9.8 a	9.8 a	6.6 a	9.7 a
Field Experiment (Soil Surface Tarped with HDPE)						
15	30	1	2.6 a	3.2 a	1.6 a	
30	30	1	1.9 a	1.8 a	0.02 b	

[a] Values are the mean of three (sand mesocosms) or two (field experiment) replicates. Values for each fumigant in each experiment followed by different lower case letters indicate statistical difference ($\alpha = 0.05$) by Tukey's mean separation test.

TABLE 2. Maximum Flux (μg m^{-2} s^{-1}) of Fumigants from Soil under Different Application Conditions[a]

treatment depth (cm)	emitter spacing (cm)	lines	cis-1,3-D	trans-1,3-D	MITC	propargyl bromide
Sand Mesocosm Experiment 1 (Bare Soil Surface)						
15	30	1	46.4 a	30.5 a	8.2 a	59.8 a
15	15	1	37.9 a	26.8 a	8.3 a	60.6 a
30	30	1	17.8 b	10.5 b	2.7 b	27.8 b
30	15	1	13.8 b	8.8 b	2.6 b	35.0 b
Sand Mesocosm Experiment 2 (Bare Soil Surface)						
15	30	1	17.4 a	11.2 a	2.9 b	22.1 a
15	30	2	18.6 a	12.8 a	4.9 a	30.8 a
Field Experiment (Soil Surface Tarped with HDPE)						
15	30	1	3.0 a	3.7 a	1.4 a	
30	30	1	1.3 a	1.1 a	0.08 a	

[a] Values are the mean of three (sand mesocosms) or two (field experiment) replicates. Values for each fumigant in each experiment followed by different lower case letters indicate statistical difference ($\alpha = 0.05$) by Tukey's mean separation test.

for PrBr (17). Thus, MITC partitions less into the soil gas phase, limiting its gas-phase diffusion, resulting in lower emissions under the same conditions.

Sand mesocosm experiments indicated that application depth had the strongest effect on cumulative emissions of all fumigant compounds applied to bare soil. Other application variables, including the emitter spacing and number of drip lines, did not significantly affect cumulative emissions of any fumigant (Table 1). In both the sand mesocosm and field experiments, cumulative emissions were consistently lower for fumigants applied at 30-cm depth compared to 15-cm depth, but this effect was statistically significant only for MITC (Table 1). In the sand mesocosm experiment, cumulative emissions of 1,3-D and PrBr were reduced by <20%, and volatilization of MITC was reduced by ~20−40% by increasing the depth of application to 30 cm. In the field experiment, increasing the depth of application drastically reduced MITC cumulative emissions, with almost no volatilization observed for HDPE-tarped, 30-cm-deep application; reported values for 1,3-D applied at 30 cm were ~60−70% of those for 15-cm application (Table 1).

Increasing the emitter spacing from 15 to 30 cm had no significant effect on the timing or magnitude of the maximum flux of any fumigant (Table 2). Likewise, applying the fumigants through two drip lines spaced 30 cm apart rather
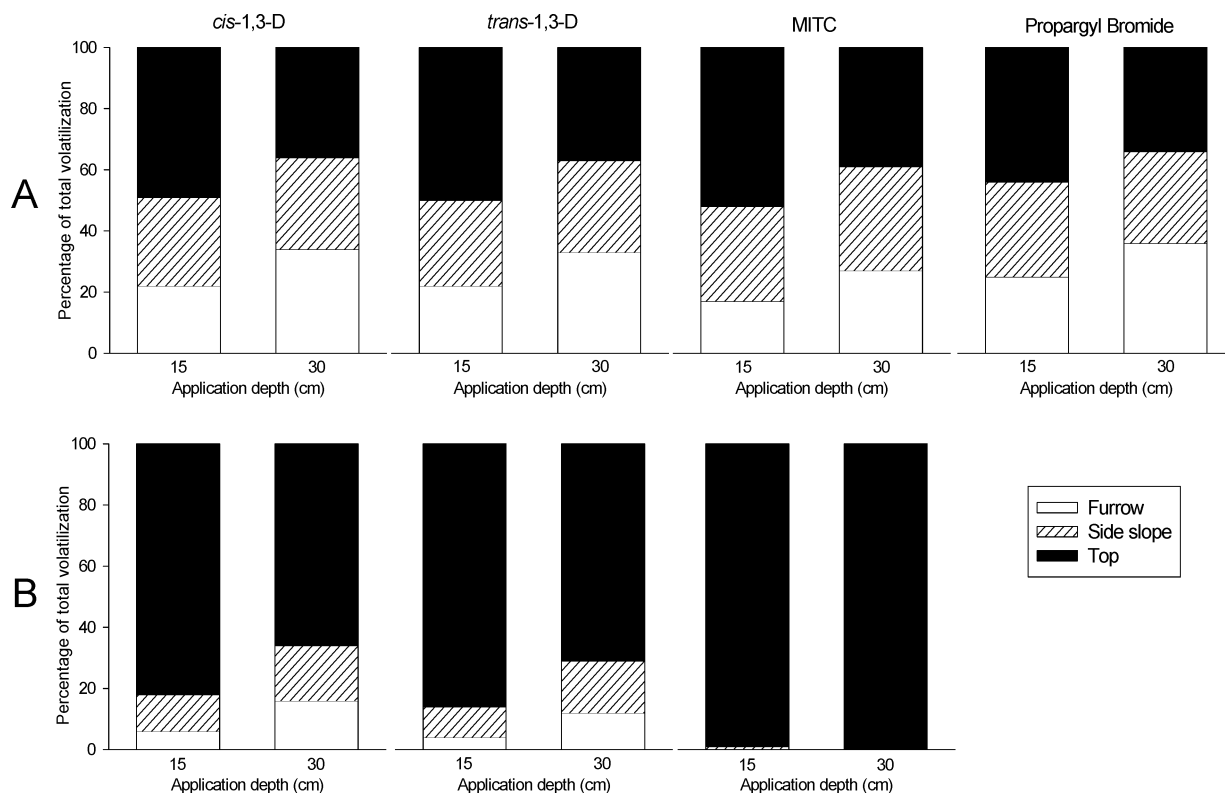
FIGURE 3. Proportion of the total fumigant flux occurring from the bed top, side slope, and furrow in the (A) first sand mesocosm experiment and (B) field experiment.
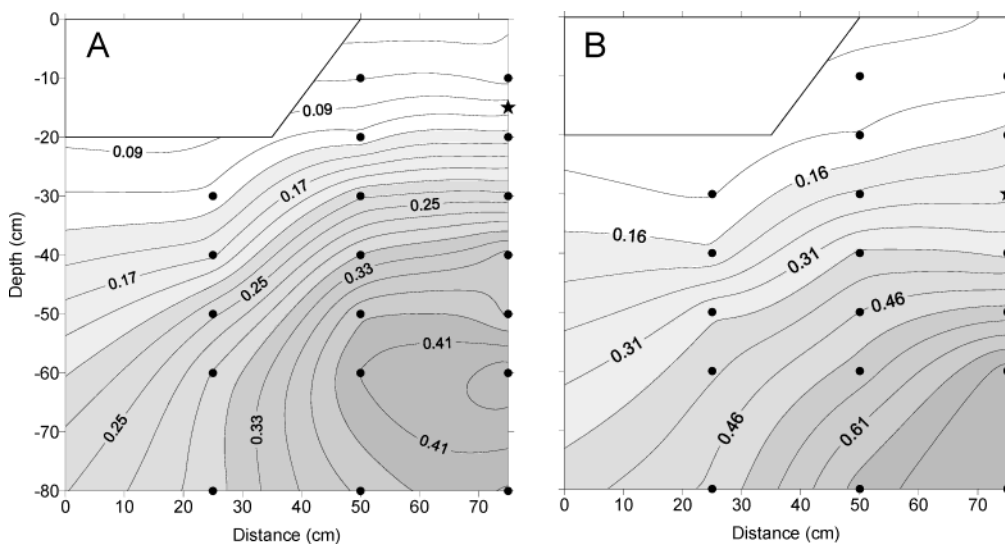

FIGURE 4. Concentration of propargyl bromide in the sand mesocosms for application at (A) 15-cm depth and (B) 30-cm depth 4 d after fumigant application. Stars indicate the location of subsurface drip irrigation lines used to apply fumigants. Propargyl bromide concentration was measured in the soil gas phase at each point indicated by the circles. Contours were constructed by kriging.

than through a single drip line at the center of the bed had no impact on the timing or magnitude of maximum flux (Table 2). However, in both the sand mesocosm and field experiments, increasing the depth of application from 15 to 30 cm significantly increased the time interval between application and the peak flux (Figure 2). Maximum flux of 1,3-D isomers and PrBr occurred 2−3 h after application for beds with drip lines installed at 15-cm depth in both the sand mesocosm and field experiments. For 30-cm-deep drip application, the maximum flux was delayed to 6−11 h (sand mesocosms) or to 28 h after application (field experiment). Increasing the depth of application also tended to reduce the magnitude of the maximum flux, but this effect was only

statistically significant for the sand mesocosm experiments (Table 2, Figure 2). The magnitude of the maximum 1,3-D flux was decreased by ~60−70%, and the maximum flux of PrBr was decreased by 40−50% by increasing the depth of application.

Maximum flux of MITC was of lower magnitude and occurred significantly later following application compared to maximum flux of 1,3-D isomers and PrBr. Maximum flux of MITC occurred 3−7 h after application for beds with drip lines installed at 15-cm depth; for 30-cm depth, maximum flux occurred at 26−52 h after fumigant application (Figure 2). Increasing the depth of application resulted in a decrease in the magnitude of the maximum MITC flux by ~70% in the
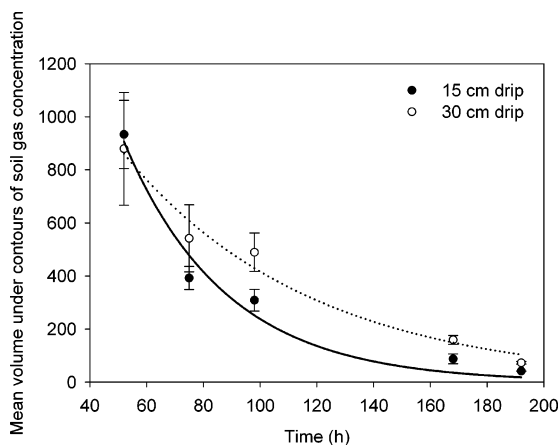
FIGURE 5. Dissipation of *cis*-1,3-dichloropropene in the first sand mesocosm experiment. Values are the mean of two mesocosms with drip tubing at the same depth, and error bars indicate the standard error. The volume under the contours of soil gas concentration was used as an indicator of the mass remaining in the monitored zone. Lines indicate the exponential decrease in mass with time.

sand mesocosm studies and by >90% in the field experiment (Figure 2, Table 2). In all experiments, maximum flux (μg m^{-2} s^{-1}) followed the trend PrBr > *cis*-1,3-D > *trans*-1,3-D > MITC. The observed difference in maximum flux (PrBr ≥ 2 times greater than 1,3-D and ~8 times more than MITC) is larger than that explained by the difference in application rate alone (81 kg ha^{-1} PrBr, 77 kg ha^{-1} 1,3-D, and 46 kg ha^{-1} MITC), and is also the result of differences in volatility, soil distribution, and rates of transformation among the fumigant compounds.

Monitoring fumigant flux from all bed dimensions (top, side slope, and furrow) indicated that emitter spacing and application through a single or double drip line had no significant impact on the pattern of fumigant emissions. Increasing the depth of application decreased the fumigant flux (expressed as the percentage of applied fumigant) from the bed top; this effect was statistically significant for all fumigants in the sand mesocosm study and for MITC in the

field experiment. Flux from the side slope and furrow was not significantly impacted by changing the application depth. Thus, increasing the depth of application decreased fumigant flux in these experiments by decreasing the flux from the bed top. The proportion of the total fumigant flux occurring from the bed top was higher for the shallower application (Figure 3). Although the flux from the furrow (expressed as a percentage of the applied fumigant) was not significantly affected by application depth, the proportion of total flux occurring from the furrows increased with increasing depth of application (Figure 3). As was observed in other experiments (*12*), the proportion of MITC flux from the furrows was lower than that for the other fumigants, and flux from the furrows was negligible in the field experiment (Figure 3).

The extent of emissions reduction achieved by increasing the depth of subsurface drip application will depend on the increase in soil residence time resulting from the increased path length to the soil surface and the rate of fumigant degradation in the soil. Conditions favoring the rapid transformation of fumigants, such as a high-organic-matter soil, may increase the effectiveness of deep soil application (*4*). Conditions favoring rapid gas-phase diffusion, such as fumigation during hot, dry conditions, may reduce the effect of deep application.

Fumigant Distribution. Increasing the depth of application tended to result in higher concentrations of fumigants in the soil gas phase several days after application (Figure 4). Fumigant application at 15-cm depth resulted in relatively rapid flux from the soil surface, depleting concentrations remaining in the soil. Fumigant volatilization was delayed in the 30-cm application because of the longer diffusive path length from the point of application to the soil surface. Deeper application also resulted in a slight reduction in fumigant emissions, since the longer residence time in soil allowed for a larger proportion of the fumigant to undergo transformation prior to volatilization. Increasing the depth of injection was less effective in containing fumigants in the soil compared to the use of a virtually impermeable film or HDPE as a surface cover (results in ref *12*).

Monitoring the soil gas distribution in the sand mesocosm experiments indicated that increasing the depth of application slowed the rate of fumigant dissipation from the root
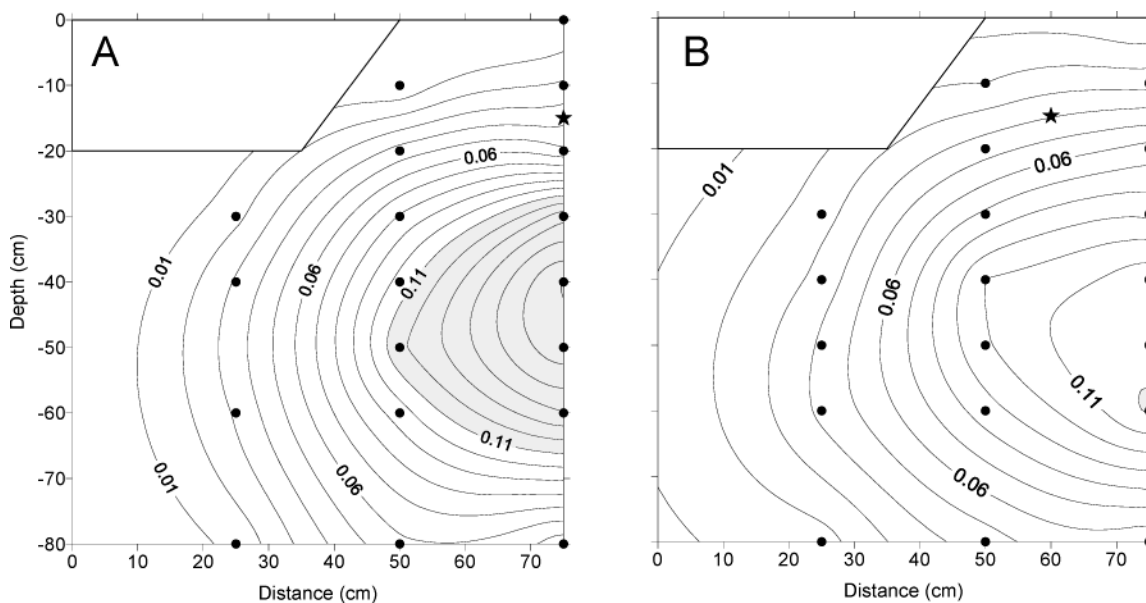

FIGURE 6. Concentration of methyl isothiocyanate (MITC) 7 d after Vapam application through (A) a single drip irrigation line at bed center and (B) two drip irrigation lines, each 15 cm from the bed center. Stars indicate the location of subsurface drip irrigation lines used to apply fumigants. Concentration of MITC was measured in the soil gas at each sampling point (indicated by circles). Contours were constructed by kriging.

zone. Integrating the volume under the contours of soil gas concentration indicated that the mass remaining in the monitored zone of beds with 30-cm-deep drip application was slightly greater than that in beds with 15-cm-deep drip application beginning 3 days after application (Figure 5). Dissipation (including losses due to volatilization and other transport out of the monitored zone, transformation, and phase partitioning) of all fumigant compounds resulted in an exponential decrease in fumigant mass in the soil gas. The change in volume under the soil gas concentration contours as a function of time was described using a first-order kinetic model (Figure 5). The first-order dissipation rate coefficient was from 1.6 (MITC) to 1.9–2.0 (1,3-D and PrBr) times greater for 15-cm-deep application than for 30-cm-deep application, indicating that the deeper application maintained higher soil gas concentrations in the monitored zone for a longer period after application. However, soil gas concentrations of 1,3-D and PrBr in the deep application generally increased with depth (Figure 4), which may have implications for achieving uniform efficacy. In both sand mesocosm experiments, the maximum concentration of all fumigants in the soil air was detected well below the depth of application beginning with the first sampling time, 1–2 days after application (Figures 4 and 6). This may be partially due to atmospheric emissions depleting the concentration of fumigants in the soil air at shallow depths. In these coarse-textured soils, appreciable downward movement of the injected solution occurred, which moved the center of mass deeper in the soil profile. Concentrations of 1,3-D and MITC also tend to increase with depth when irrigation water is applied following fumigant application (*18*). These results suggest that in coarse-textured soils, downward movement of fumigants applied with irrigation water may result in the leaching of fumigants below the root zone, possibly leading to decreased pest-control efficacy and contamination of shallow groundwater.

Studies conducted concurrently with these experiments in sand mesocosms and the field site indicated that MITC was not uniformly distributed across the bed, even long after application, when applied through a single irrigation line at the center of the bed (*12*). One approach considered for increasing the uniformity of MITC distribution is the application of metam sodium through two drip lines in a single bed. In these sand mesocosm experiments, we investigated the distribution of MITC and other fumigants when applied to a 50-cm-wide bed through two lines spaced 30 cm apart and one line at the center of the bed. Results indicated little difference in the distribution of any fumigant in the soil gas

phase due to application conditions (Figure 6). Although both applications used the same total water volume, so that half of the total solution was passed through each of the two drip lines, the downward movement of fumigant solution was not appreciably different for the two configurations (Figure 6). Thus, it appears that for coarse-textured soils, fumigant application through multiple drip lines may not improve fumigant distribution, efficacy, or fumigant leaching.

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