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Effect of Surface Tarp on Emissions and Distribution of Drip-Applied Fumigants

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Soil fumigants are used to control a wide variety of soil-borne pests in high-cash-value crops. Application of soil fumigants through drip irrigation systems is receiving increasing attention as a method to improve the uniformity of fumigant application. Little information is available on the emissions and soil distribution of fumigants following subsurface drip application, or the effect of plastic tarp on fumigant emissions in these systems. In these experiments, the fumigant compounds 1,3-dichloropropene (1,3-D), Vapam (a methyl isothiocyanate (MITC) precursor), and propargyl bromide (PrBr) were applied to soil beds via drip irrigation at 15 cm depth. Beds were tarped with either standard 1-mil high-density polyethylene (HDPE) or a virtually impermeable film (VIF), leaving the furrows bare. Cumulative emissions of 1,3-D, MITC, and PrBr in these tarped bedded systems was very low, amounting to <10% of the applied mass. These experiments were conducted in the winter months, with average air temperatures of 12−15 °C. Cumulative emissions of MITC and 1,3-D from a sandy loam field soil were decreased by ≥80% by tarping the bed with VIF rather than HDPE. A large fraction of the 1,3-D and PrBr flux was from the untarped furrows in VIF-tarped plots, indicating that inhibiting volatilization from the furrow will be important in further reducing emissions in these systems. Monitoring the fumigant distribution in soil indicated that tarping the bed with VIF resulted in a more effective containment of fumigant vapors compared to use of a HDPE tarp.

Introduction

Fumigants are used for the control of soil-borne pests and pathogens in high-cash-value crops. Currently available fumigant compounds include 1,3-dichloropropene (1,3-D), chloropicrin (CP), and methyl isothiocyanate (MITC). Other efficacious compounds have been proposed for use as soil fumigants, including iodomethane (methyl iodide) and propargyl bromide (PrBr). All fumigants have relatively high vapor pressures, low boiling points, and high air−water partitioning coefficients (K_H). Thus, fumigants have high mobility in the vapor phase, are rapidly dispersed through soil, and are prone to volatilization from the soil surface following application to soil. For example, volatilization of 1,3-D measured in field plots has exceeded 30% of the applied fumigant (*1*). Regulations restrict fumigant application because of the adverse human and environmental health effects resulting from their presence in air.

Several approaches have been proposed to reduce the atmospheric emissions of fumigants following application to soil. Restricting gas-phase diffusion in the soil can decrease emissions by increasing the time available for fumigant transformation in the soil. Increasing soil bulk density and increasing the initial soil moisture have been demonstrated to reduce fumigant emissions (*2*). Applying fumigants with water through drip irrigation lines has been proposed as a means to decrease emissions by the same principle (*3*−*4*). Use of a surface seal has also been demonstrated to reduce emissions by decreasing the rate of transport across the soil−air interface. Surface application of water can form a diffusion barrier at the soil surface and decrease emissions (*4*−*7*). Plastic films are routinely used to inhibit volatilization. Standard 1-mil high-density polyethylene (HDPE) is permeable to fumigant compounds (*8*−*9*), resulting in the loss of a large proportion of the applied fumigant through atmospheric emissions (*10*−*11*). Lower-permeability films have been developed, and the use of virtually impermeable films (VIFs) has been demonstrated to significantly reduce fumigant emissions. For example, emissions of the fumigants methyl bromide and CP may be nearly eliminated when a VIF forms a continuous cover that remains intact long enough to allow for complete transformation of the fumigant in soil (*12*−*13*).

Application of 1,3-D through drip irrigation systems can result in relatively uniform concentrations of 1,3-D throughout the soil profile (*3*, *14*). Soil application of metam sodium often does not result in uniform distribution of MITC, which may limit its efficacy (*15*). Several studies have indicated that use of a VIF increases soil gas concentrations of fumigants applied via shank (*12*) or surface drip application (*3*), suggesting that decreased fumigant application rates may provide sufficient pest control efficacy.

Although much published information is available discussing the emissions of the fumigant methyl bromide (*16*), less information is available for the alternative fumigants, including 1,3-D and MITC. Few detailed studies of fumigant emissions following application by subsurface drip irrigation systems have been reported. Little information exists discussing the effect of surface tarp on emissions and distribution of 1,3-D, MITC, and PrBr. The objectives of these experiments were to investigate the emissions and soil distribution of 1,3-D, MITC, and PrBr following subsurface drip application in bedded systems in which the bed was tarped with 1-mil HDPE or with a VIF.

Materials and Methods

Chemicals. 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 Corporation (Los Angeles, CA). Propargyl bromide (80% in toluene) was provided by Albemarle Corporation (Baton Rouge, LA). InLine and Vapam are commercial fumigant formulations labeled for application by subsurface drip. Propargyl bromide is an experimental product not registered for use as a soil fumigant. Analytical standards of

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TABLE 1. Physical and Chemical Properties of Fumigant Compounds at 20 °C

fumigant	boiling point[a] °C	vapor pressure[a] mmHg	Henry's law constant (K_H)[a]	water solubility[b] mg L^{-1}
cis-1,3-D	106	25	0.056	2700
trans-1,3-D	111	18.5	0.041	2800
MITC	119	20	0.010	7600
propargyl bromide[c]	89	48.4	0.037	14800

[a] Data for 1,3-D isomers and MITC from ref. *16*. [b] Data for 1,3-D isomers from ref. *24*; MITC data from ref. *3*. [c] Propargyl bromide data from ref. *25*.

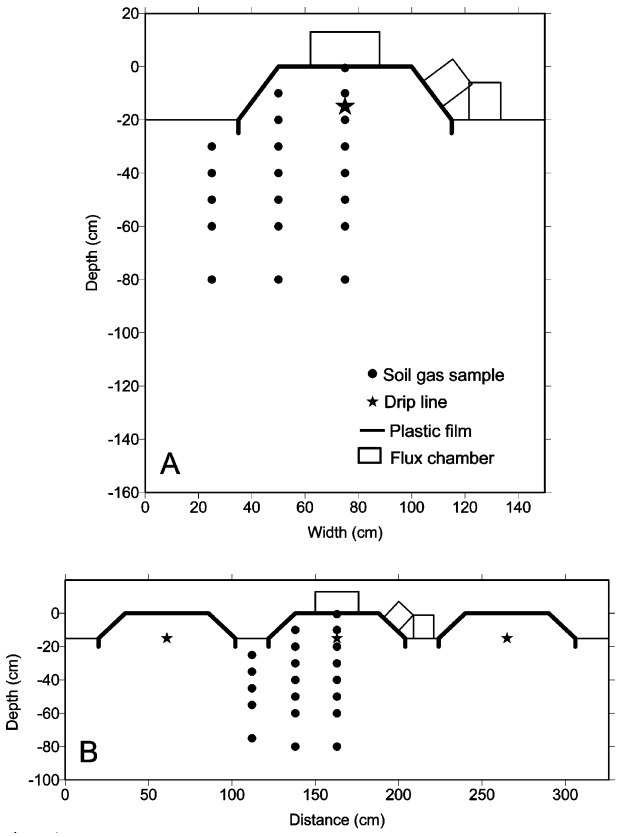

FIGURE 1. Schematic diagrams indicating the dimensions of the beds in the (A) sand mesocosm and (B) field experiments, the locations of drip lines, placement of flux chambers, locations of soil gas samples, and placement of plastic film on the beds.

1,3-D and MITC were purchased from ChemService (West Chester, PA). Selected physical and chemical properties of 1,3-D isomers, PrBr, and MITC are given in Table 1.

Plastic Films. A sample of HDPE currently used in soil fumigation was obtained from TriCal, a commercial fumigant applicator. Hytibar, a VIF, was provided by the manufacturer (Klerk's Plastics, Belgium). Both films had a nominal thickness of 1.5 mil (0.038 mm).

Sand Mesocosm Experiments. Experiments were conducted March 4−12, 2002 in concrete mesocosms (3 m long × 1.5 m wide × 1.6 m deep, Figure 1A) filled with washed river sand to a bulk density of 1.7 Mg m^{-3}. 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 at the center of each bed to a depth of 15 cm. Drip irrigation tubing (16-mm diam HDPE) with built-in emitters at 30-cm spacing and a flow rating of 3.8 L h^{-1} was placed in the trench. The trench was backfilled, the bed was re-shaped, and the soil surface was packed by tapping with a flat board. Plastic tarp (1-mil HDPE or Hytibar) was placed over the bed surface, and the edge of the plastic was buried ∼5 cm into the soil at the edge of the bed (Figure 1A). Each tarp was used in triplicate mesocosms.

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). 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 ∼3 h, and carboys were shaken periodically to maintain a uniform solution concentration. Following fumigant application, 4 L of fresh water was added to each plastic carboy and injected through the drip lines to rinse the system.

A weather station was installed on-site to monitor air temperature, relative humidity, and precipitation during the experiment. The mean air temperature was 14.5 °C (range 6−27 °C), the mean relative humidity was 47.0% (range <10−92%), 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 soil was an Arlington sandy loam (coarse-loamy, mixed, thermic, Haplic Durixeralf) comprised of 75% sand, 18% silt, and 7% clay; the organic carbon content of this soil is 9.2 g kg^{-1} and the pH is 6.7. The experiments were conducted from December 9−16, 2002. The mean air temperature during the experiment was 11.6 °C (range 2−22 °C) and the mean relative humidity was 70% (range 20−97%); there was no measurable precipitation during the flux experiment. Beds were formed, measuring 15 cm high and 50 cm across the top with 20-cm furrows (Figure 1B); rows were 10 m long. Drip line was mechanically installed in each bed at a nominal depth of 15 cm. Beds receiving HDPE were tarped by machine; Hytibar was laid manually. Flux was monitored on the center row of three rows with the same plastic tarp, with the outside rows acting as buffers between treatments (Figure 1B). Duplicate test rows were used for each tarp, and treatments were arranged in a completely randomized design.

Fumigants were added at the same rate as in the sand mesocosm experiments, except that PrBr was not included because of a lack of available material. Measured amounts of fumigants (3.6 L of InLine and 5.9 L of Vapam) were poured into 190 L of water in a closed commercial polyethylene mixing tank and continuously stirred by a stainless steel impeller. The fumigant−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 3 m of 5-cm diam PVC pipe (turbulent flow), then split into two 2.5-cm diam PVC pipes. The fumigant solution was passed through a pressure regulator set at 11 psi and 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. (The experiments reported here used 12 of the 30 treated beds.) Drip lines were 16-mm polyethylene lines with 3.8 L h^{-1} emitters with a 30-cm spacing between emitters. 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 fresh water was added to the drip irrigation system to rinse the lines.

Monitoring Emissions. Volatilization was measured using metal passive chambers, which have been previously used for measuring fumigant flux in field studies (*17*). Passive chambers had an open bottom and 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 plastic tarp, with the outside rows acting as buffers between treatments (Figure 1B). Chambers used to measure volatilization from the top of the bed were 13 cm high and covered a surface area of 1077 cm^2. Smaller chambers were required to fit the dimensions of the side slope and furrow; these chambers were 14 cm high and covered a surface area of 522 cm^2. Chambers were placed on the soil surface for 30 min, during which time the fumigant concentration in the chamber increased with time due to the chemical moving from the soil into the chamber. Samples (100 mL) were then removed through a sampling port in each chamber. Syringes were used to apply vacuum and to measure the sample volume. An adsorbent tube was placed between the chamber and the syringe to extract the fumigants from the air stream. Activated coconut charcoal tubes containing two sections of adsorbent (100 and 50 mg) separated by glass wool were used in the sand mesocosm experiments; XAD adsorbent tubes containing two sections of adsorbent (40 and 80 mg) were used in the field study. Preliminary experiments indicated no breakthrough of fumigants using these low sample volumes. 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 in a 10-mL vial, which was placed on a reciprocating shaker for 1 h. 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 μ-ECD (1,3-D and PrBr) or NPD (MITC).

Volatilization fluxes ($\mu g\ m^{-2}\ s^{-1}$) 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_c is the chamber volume (mL), V_s is the volume of gas removed from the chamber (100 mL), A is the chamber base surface area (m^2), and T_s is the chamber placement time (30 min or 1800 s). Flux was monitored for 194 h in the sand mesocosm experiment and for 170 h in the field experiment. Fluxes were integrated over time and space to give an estimate of the total volatilization (as a percentage of the applied mass). For MITC, calculations were based on 100% conversion of metam sodium to MITC. Fluxes were calculated for each bed dimension (top, side slope, and furrow) to provide a measurement of the total flux at each measurement time. Flux was further characterized by calculating the maximum flux, the time of maximum flux, and the flux occurring in the first 40 h after application.

Monitoring Fumigant Distribution in Soil. Teflon tubing (1-mm i.d.) was buried vertically following bed formation but prior to tarping. Tubes of the same length were terminated from 20 to 80 cm below the soil surface throughout half of the bed cross-sectional area (Figure 1) to provide information on the distribution of fumigant compounds in the root zone. Soil gas samples were collected on the opposite side of the row from flux samples (Figure 1) to avoid disrupting the gas sampling tubes during flux chamber placement. In the field study, fumigant distribution was monitored on the center row of triplicate treated rows with the same plastic tarp (Figure 1B). Gas samples (50 mL) were collected on adsorbent tubes (activated charcoal in the sand mesocosm experiment, XAD in the field experiment). Syringes were used to apply vacuum and to measure the gas volume sampled. This approach has been successfully used in previous experiments to monitor soil gas concentrations (*6*). Fumigant compounds were extracted and analyzed as described above. Soil gas concentrations of fumigants were measured 1, 2, 3, 4, 7, and 8 d after fumigant application in the sand mesocosm experiments and 1, 2, 4, and 7 d after fumigant application in the field experiment. Concentration data were kriged to construct contour maps of soil gas concentrations throughout the soil profile. The volume under the concentration contours was determined to estimate the mass of fumigant remaining in the monitored zone of each bed at each sampling time.

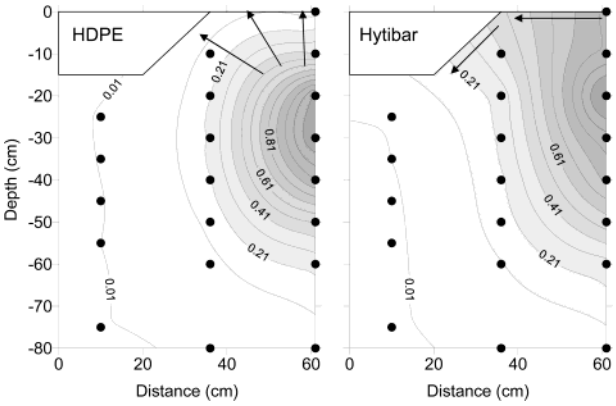

FIGURE 2. Concentration ($\mu g\ cm^{-3}$) of *cis*-1,3-dichloropropene in the soil gas measured in the field experiments 2 days after fumigant application. Contours were constructed by kriging. Points indicate locations of soil gas samples. Arrows indicate the approximate direction of fumigant transport, perpendicular to the concentration gradient.

Statistical Analyses. Response data including the cumulative emissions, maximum flux, time to maximum flux, flux occurring in the first 40 h after application, and flux from the bed top, side slope, and furrow were subjected to statistical analyses. Each experiment was set up as a one-way ANOVA model, with surface tarp (HDPE or Hytibar) as the fixed effect factor. Four fumigant compounds (*cis*-1,3-D, *trans*-1,3-D, PrBr, and MITC) were measured on each response variable; therefore, the response data were analyzed using a one-way multivariate analysis of variance (MANOVA) model. The field experiment data were 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 surface treatments was tested by first performing a MANOVA test for treatment differences across all four fumigants simultaneously (*18*). 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 (*19*).

Results and Discussion

Distribution in Soil. Tarping the bed with Hytibar resulted in the maintenance of higher fumigant concentrations in the soil compared to those of HDPE-tarped soil. Soil concentrations under Hytibar were generally greater than those under standard 1-mil HDPE, especially near the soil surface (Figure 2). For example, the mean soil gas concentration measured in the sand mesocosms 8 days after fumigant application was 2 (MITC) to >4 (*cis*- and *trans*-1,3-D) times greater in beds tarped with Hytibar than in beds

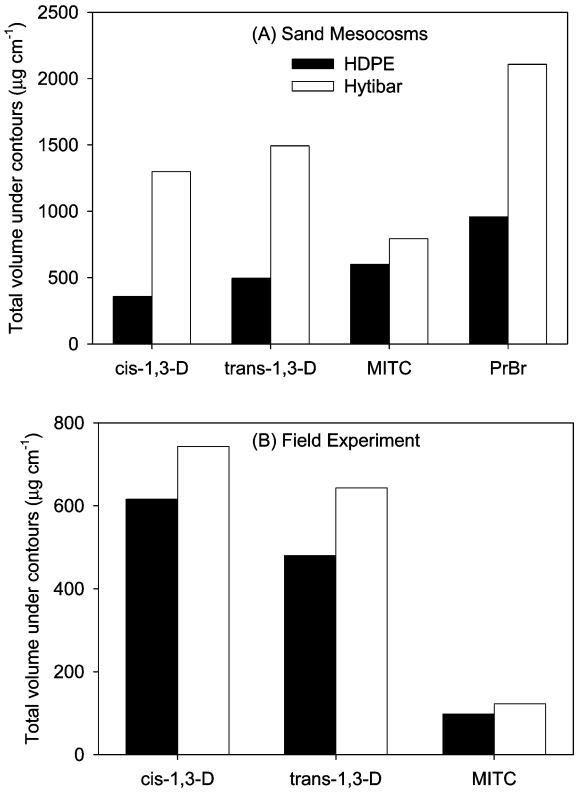

FIGURE 3. Estimate of mass remaining in soil (calculated by the total volume under the contours) in the (A) sand mesocosm and (B) field experiments 4 days after fumigant application.

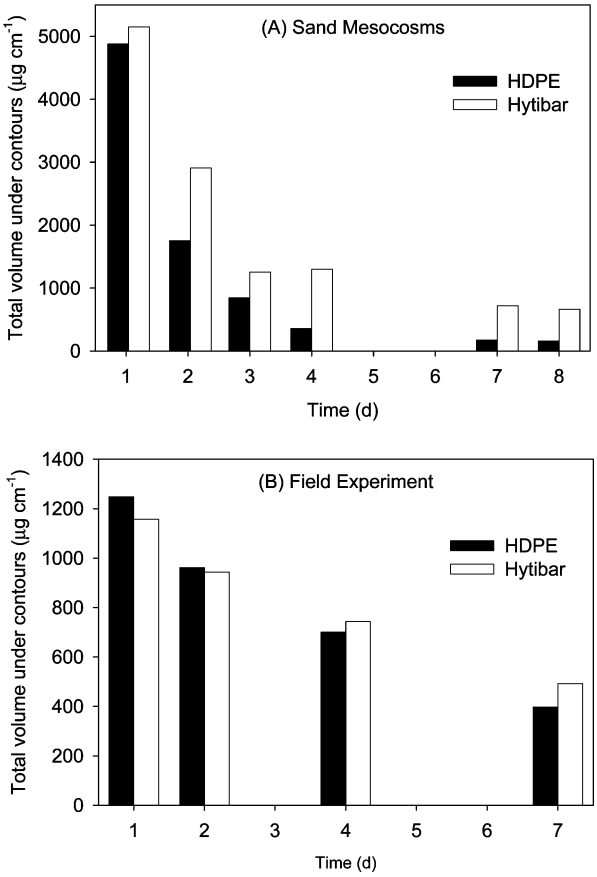

FIGURE 4. Dissipation of *cis*-1,3-dichloropropene in the (A) sand mesocosm and (B) field experiment as indicated by the estimated mass remaining in soil (calculated by the total volume under the contours).

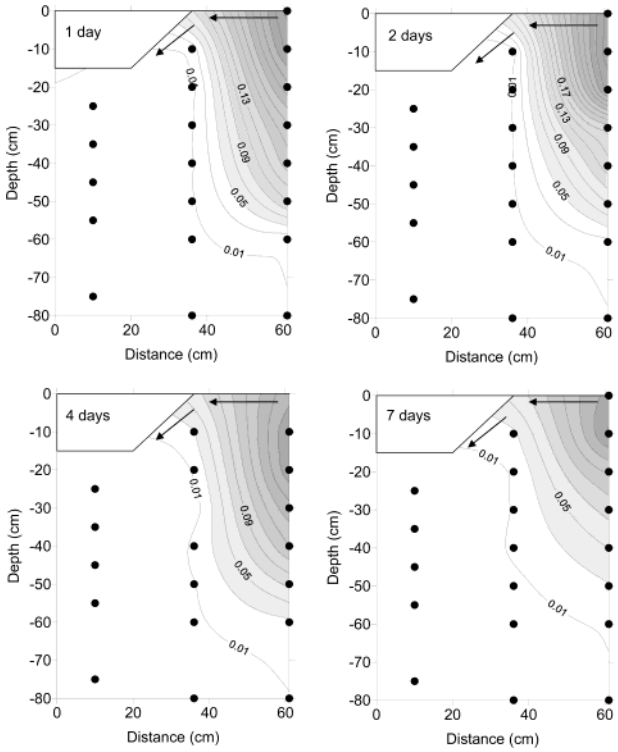

FIGURE 5. Concentration (μg cm^{-3}) of MITC in the soil gas in Hytibar-tarped beds in the field experiment. Contours were constructed by kriging. Points indicate locations of soil gas samples. Arrows indicate the approximate direction of fumigant transport, perpendicular to the concentration gradient.

tarped with 1-mil HDPE. Previous studies using drip application of 1,3-D also showed higher concentrations remaining in the soil 24 h after application with use of a VIF compared to those with use of a standard HDPE (*3*).

Integrating the volume under the concentration contours provided an estimate of the fumigant mass remaining in the monitored zone. The results demonstrated that Hytibar was more effective than HDPE at containing fumigant vapors in the soil (Figure 3). Better containment with use of a VIF could result in greater pest-control efficacy and may provide adequate pest control with reduced fumigant application rates (*12*). Fumigant dissipation from soil (Figure 4) generally followed first-order kinetics; results indicated that fumigants in beds tarped with Hytibar were more slowly dissipated in soil (longer half-life) compared with fumigants in HDPE-tarped beds because of the rapid loss of fumigants from HDPE-tarped soil via volatilization. Numerous processes are reflected in the dissipation of fumigants from the soil gas phase, including transformation, phase partitioning, and volatilization. High fumigant concentrations remaining in soil at planting can result in crop phytotoxicity (*20*). Soil fumigation using VIF should allow sufficient cover times to allow for complete fumigant transformation in the soil prior to disrupting the tarp (to avoid fumigant escape to the atmosphere) and planting (to avoid crop damage by residual fumigants).

Fumigant distribution in Hytibar-tarped soil demonstrated a small vertical concentration gradient near the soil surface compared to that in HDPE-tarped soil (Figures 2 and 5). The low permeability of Hytibar to fumigant vapors resulted in the maintenance of high fumigant concentrations under the tarp, which may be released to the atmosphere if the film is removed prior to complete fumigant transformation in the soil (*13*). Concentration gradients in Hytibar-tarped soil indicate that the fumigant transport is directed toward the untarped furrow (Figures 2 and 5). Because of the

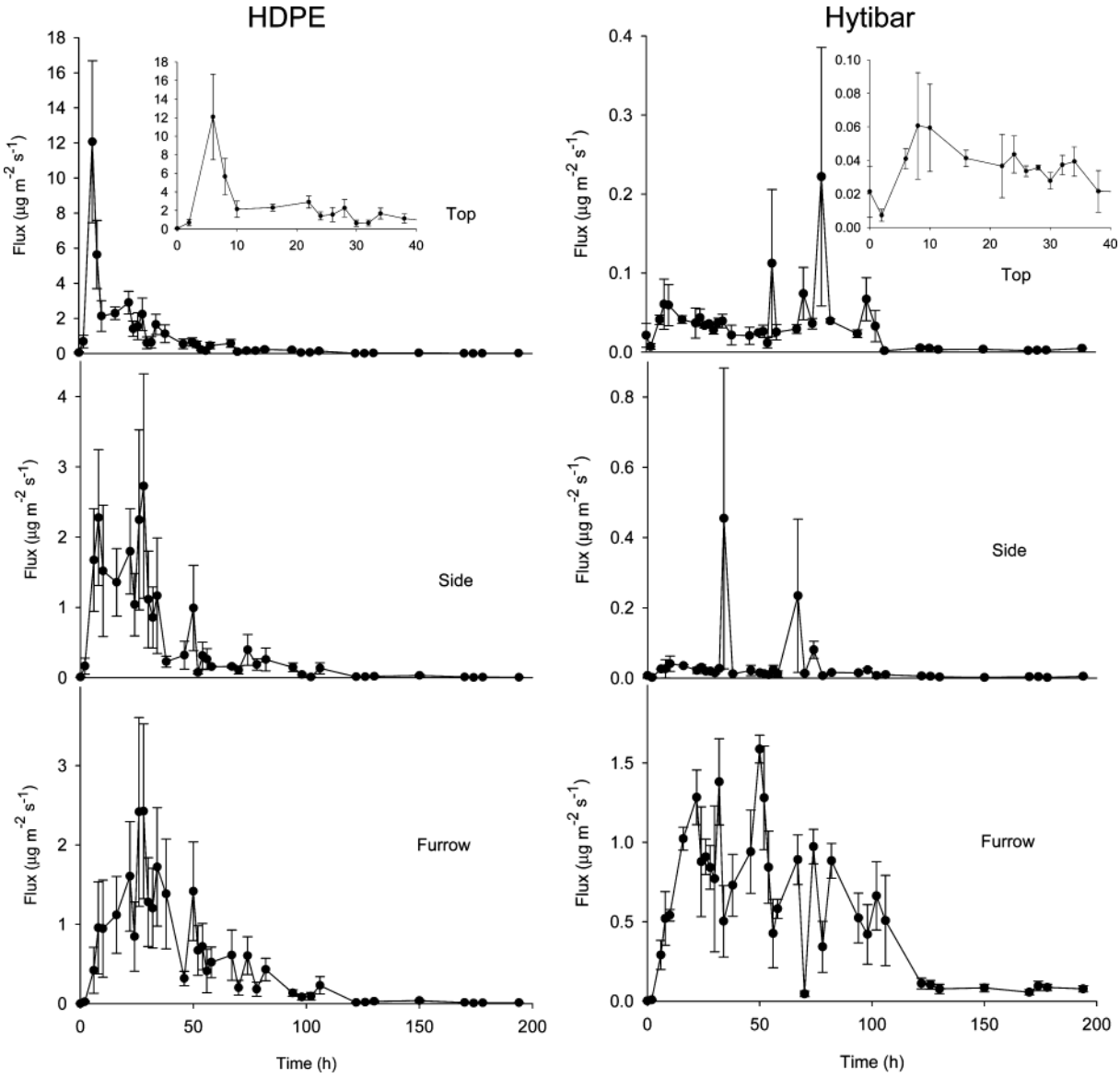

FIGURE 6. Flux of *cis*-1,3-dichloropropene in the sand mesocosm experiment. Values indicate the mean (± standard error) of triplicate sand mesocosms. Insets indicate flux from the top of the bed in the first 40 h after application.

relatively high permeability of 1-mil HDPE to fumigant vapors, the vertical concentration gradient at the soil surface is large and fumigant concentrations directly under the tarp are lower than those under Hytibar (Figure 2). Concentration gradients in HDPE-tarped soil indicate that the fumigant transport radiates from the maximum concentration, and is not appreciably restricted by the tarp (Figure 2).

In samples of soil gas, the concentration of *cis*-1,3-D was consistently higher than that of *trans*-1,3-D. This is consistent with the physical chemical properties of the two isomers (Table 1), which indicate that *cis*-1,3-D is slightly more volatile and partitions into the vapor phase to a greater extent (higher K_H) than *trans*-1,3-D. This isomeric trend has been observed in previous studies of 1,3-D distribution in soil (*14*). Monitoring the distribution of MITC indicated that concentrations away from the bed center were very low (Figure 5). Restricted transport of MITC may result from its limited transport in the gas phase—MITC has a relatively low Henry's Law constant and high water solubility (Table 1). Thus, MITC is expected to be present primarily in the aqueous phase, and MITC may not be distributed throughout the bed to the same extent as the other fumigants used in this study.

The spatial variance in soil gas concentration measured at a single time was used as a measure of the uniformity of fumigant distribution, as all fumigant compounds were measured in a single gas sample (no spatial or temporal change in sample location). For all fumigants, the spatial variance in soil gas concentration decreased exponentially with time. The variance in MITC concentration decreased at a slower rate than the variance in 1,3-D and PrBr concentration: the rate of change in variance was 2−5 times greater for 1,3-D isomers and PrBr than for MITC in both experiments. Thus, 1,3-D and PrBr concentrations equalized throughout the monitored profile more quickly than MITC concentrations did. The spatial variance in 1,3-D and PrBr concentration was very low in tarped soil within a few days after application, indicating a relatively uniform concentration across the bed by 3−4 days after application. Low MITC concentrations outside the bed could result in poor pest-control efficacy in furrows, and alternative strategies for MITC application (or alternative pest control methods) may be required.

Fumigant Emissions. *1,3-D.* Volatilization from the soil surface began soon after fumigant application and continued for days following application (Figure 6 and 7). In the sand

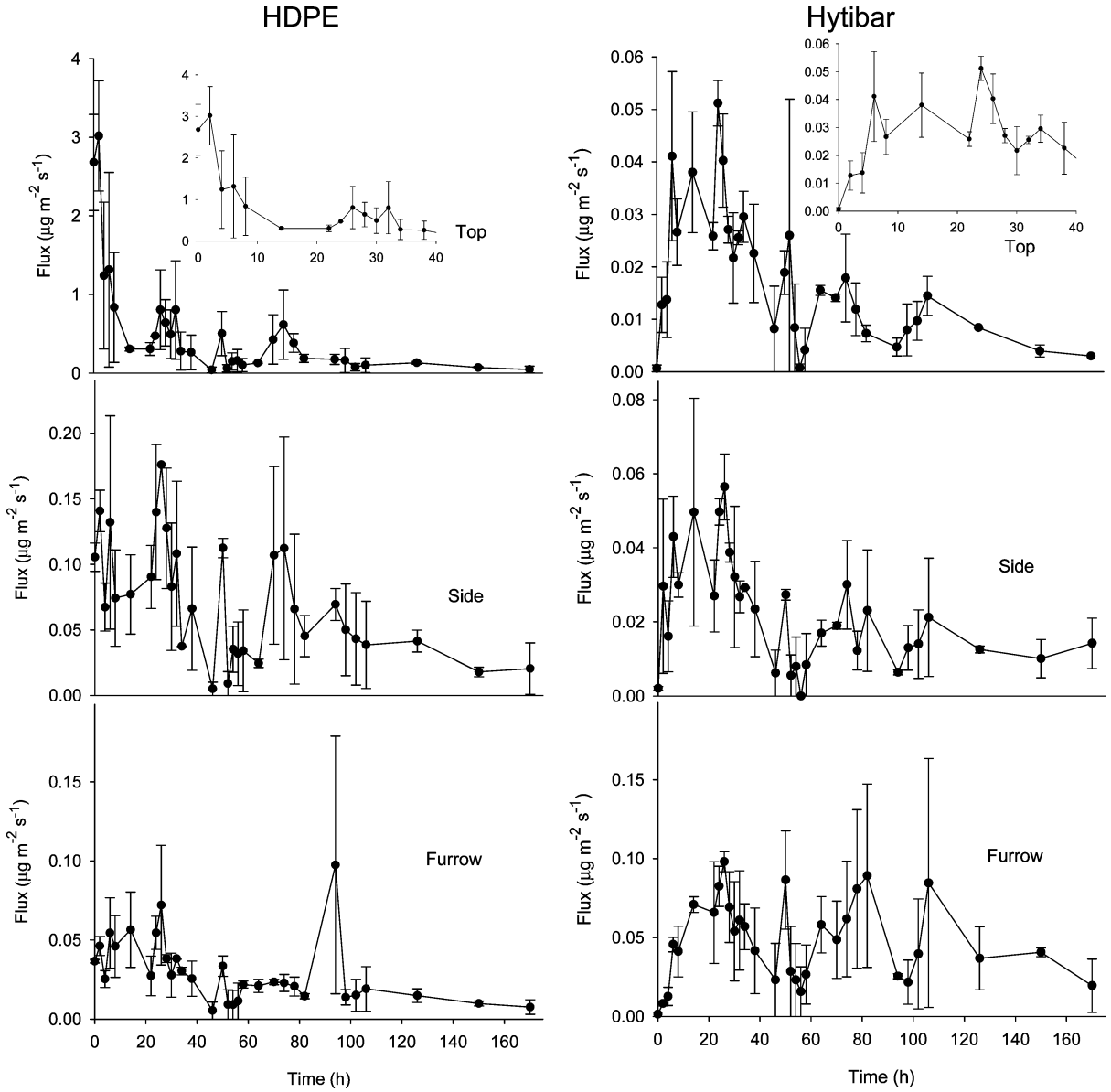

FIGURE 7. Flux of *cis*-1,3-dichloropropene in the field experiment. Values indicate the mean (± standard error) of duplicate rows. Insets indicate flux from the top of the bed in the first 40 h after application.

TABLE 2. Cumulative Emissions of Fumigant Compounds (% of applied) Measured in the Sand Mescocosm and Field Experiments[a]

surface tarp	*cis*-1,3-D	*trans*-1,3-D	MITC	propargyl bromide
		sand mesocosm experiment		
HDPE	9.5 a	9.8 a	3.4 a	9.2 a
Hytibar	3.9 a	3.3 a	0.6 b	3.1 a
		field experiment		
HDPE	2.7 a	3.2 a	1.6 a	
Hytibar	0.5 b	0.4 b	0.005 b	

[a]Values for each fumigant followed by different letters are significantly different ($\alpha = 0.05$).

TABLE 3. Maximum Flux (μg m^{-2} s^{-1}) of Fumigants Measured in the Sand Mesocosm and Field Experiments[a]

surface tarp	*cis*-1,3-D	*trans*-1,3-D	MITC	propargyl bromide
		sand mesocosm experiment		
HDPE	13.77 a	9.93 a	2.27 a	18.33 a
Hytibar	1.63 a	1.17 b	0.50 a	3.03 b
		field experiment		
HDPE	3.02 a	3.73 a	1.42 a	
Hytibar	0.14 a	0.08 a	0.04 a	

[a] Values for each fumigant followed by different letters are significantly different ($\alpha = 0.05$).

mesocosm study, tarping the bed with Hytibar rather than HDPE did not significantly ($\alpha = 0.05$) reduce the cumulative emissions of 1,3-D isomers, although the reported values are 60−70% lower for VIF (Table 2). In the field study, cumulative 1,3-D emissions from Hytibar-tarped beds was more than 80% lower than that from HDPE-tarped beds. Although not statistically significant at $\alpha = 0.05$, the maximum flux of 1,3-D was reduced by ~90% or more by tarping with Hytibar in both experiments (Table 3, Figures 6 and 7). This effect was significant for both isomers in both experiments at $\alpha = 0.10$.

Emissions of 1,3-D measured in these experiments were low, totaling ~10% of the applied 1,3-D in the sand mesocosm experiment and ~3% in the field experiment (Table 2). These cumulative emissions are lower than those measured in other

TABLE 4. Cumulative Emissions of Fumigant Compounds (% of applied) Measured in the First 40 Hours after Application in the Sand Mesocosm and Field Experiments[a]

surface tarp	*cis*-1,3-D	*trans*-1,3-D	MITC	propargyl bromide
		sand mesocosm experiment		
HDPE	7.2 a	6.0 a	1.5 a	6.1 a
Hytibar	1.4 a	1.0 b	0.01 b	0.9 a
		field experiment		
HDPE	1.6 a	1.9 a	0.8 a	
Hytibar	0.2 b	0.2 b	0.002 b	

[a] Values for each fumigant followed by different letters are significantly different ($\alpha = 0.05$).

field experiments, probably because of the cool air and soil temperatures prevalent during these experiments. Gan et al. (*17*) determined cumulative emissions of subsurface drip-applied *cis*- and *trans*-1,3-D in field plots of Carsitas loamy sand (mixed, hyperthermic Typic Torripsamments), and found that cumulative emissions from the portions of the bed tarped with HDPE were 24.6% for *cis*-1,3-D and 22.6% for *trans*-1,3-D. Those experiments were conducted in March (mean air temperature ~19 °C; mean relative humidity 33%) in sandy soil (84% sand, 13% silt, 3% clay) and are therefore expected to demonstrate higher emissions than the experiments reported here. No significant difference in the emissions of the two 1,3-D isomers was observed in these experiments. Previous laboratory and field investigations of 1,3-D emissions following application by subsurface irrigation have also indicated small differences in the instantaneous flux and cumulative emissions of the two 1,3-D isomers (*4*, *17*, *21*).

In HDPE-tarped beds in the sand mesocosm experiment, the maximum flux occurred ~7 h after application; in Hytibar-tarped beds, the maximum flux was significantly delayed to >60 h after application (Figure 6). In the field experiment, maximum flux from HDPE-tarped beds occurred in the first sample (2 h after application); in Hytibar-tarped beds, maximum flux was delayed to 15−24 h after application (Figure 7). Thus, a large fraction (60−75%) of the cumulative 1,3-D emissions occurred within the first 40 h after application for HDPE-tarped beds, whereas for Hytibar-tarped beds, only 30−35% of the cumulative emissions occurred within the first 40 h after application (Figures 6 and 7, Table 4). This effect was significant at $\alpha = 0.05$ for the field experiment and at $\alpha = 0.10$ for both experiments. Emissions from HDPE-tarped beds occurring long after application (>100 h) were low in both experiments, but accounted for 20−30% of the total emissions from Hytibar-tarped beds (Figure 6 and 7). The prolonged low-level volatilization from Hytibar-tarped soil may have implications for human and environmental health, because low daily exposures would result from this application practice. These results indicate the importance of maintaining the VIF cover as long as possible before disruption or removal, because effective containment causes slower dissipation from the soil and measurable volatilization from the soil >4 days following application (Figures 6 and 7). Removal of the VIF prior to complete transformation of the fumigant in the soil will result in an emissions spike, where fumigant trapped under the film is rapidly released to the atmosphere.

In HDPE-tarped plots in both experiments, the maximum flux of 1,3-D was greater from the bed top than from the side slope and furrow (Figures 6 and 7), and cumulative emissions were dominated by the flux from the bed top (Table 5). In contrast, the cumulative emissions of 1,3-D from beds tarped with Hytibar was dominated by the flux from the furrow (Table 5). In both experiments, cumulative emissions from the furrow (expressed as a percentage of applied 1,3-D) were the same in HDPE- and Hytibar-tarped beds (Table 5). However, very low emissions from the portions of the bed tarped with Hytibar (bed top and side slope) resulted in a large proportion of the emissions occurring from the untarped furrows (Table 5). In beds tarped with VIF in the sand mesocosm experiments, nearly all (>85%) of the 1,3-D flux came from the untarped furrows, but it should be noted that the configuration of the beds in the sand mesocosms included a furrow that is significantly wider than those commonly used in field situations (Figure 1). These results indicate that measuring flux from the bed top only (flux through the tarp) may seriously underestimate the total flux occurring from partially covered fields.

Propargyl Bromide. Emissions of PrBr in the sand mesocosms followed the same trends observed for 1,3-D, and the magnitude of emissions was similar to that of 1,3-D (Table 2). Tarping the bed with Hytibar did not significantly ($\alpha = 0.05$) reduce cumulative emissions of PrBr, although the reported values are ~30% of HDPE (Table 2). The magnitude of the maximum flux was 83% lower for Hytibar-tarped beds than for HDPE-tarped beds (Table 3). Maximum flux of PrBr occurred at 7 h for HDPE-tarped beds, but was significantly delayed to 86 h in Hytibar-tarped beds. Thus, a large fraction (66%) of the total flux occurred in the first 40 h following application for beds tarped with HDPE, but only 30% of the total emissions from Hytibar-tarped beds (Table 4, Figure 8); this effect was statistically significant at $\alpha = 0.10$. Emissions long after (>100 h) application contributed only a small portion (8%) of the cumulative emissions for HDPE-tarped beds, but 17% of the total for Hytibar-tarped beds (Figure 8).

Flux of PrBr in sand mesocosms was approximately evenly distributed between the bed top, side slope, and furrow for

TABLE 5. Cumulative Emissions (% of applied) from the Bed Top, Side Slope, and Furrow Measured in the Sand Mesocosm and Field Experiments[a]

	cis-1,3-D			*trans*-1,3-D			MITC			propargyl bromide		
surface tarp	top	side	furrow	top	side	furrow	top	side	furrow	top	side	furrow
						sand mesocosm experiment						
HDPE	4.1 a	2.1 a	3.4 a	4.0 a	1.9 a	2.7 a	1.9 a	0.9 a	0.6 a	3.00 a	1.98 a	4.27 a
	(0.43)	(0.22)	(0.35)	(0.47)	(0.22)	(0.31)	(0.53)	(0.28)	(0.18)	(0.33)	(0.21)	(0.46)
Hytibar	0.1 b	0.1 a	3.6 a	0.3 b	0.2 a	2.9 a	0.2 b	0.04 a	0.4 a	0.21 b	0.17 a	2.69 a
	(0.04)	(0.04)	(0.92)	(0.08)	(0.06)	(0.86)	(0.35)	(0.06)	(0.61)	(0.07)	(0.06)	(0.87)
						field experiment						
HDPE	2.2 a	0.3 a	0.1 a	2.8 a	0.3 a	0.1 a	1.6 a	0.02 a	0.001 a			
	(0.82)	(0.12)	(0.23)	(0.86)	(0.10)	(0.04)	(0.99)	(0.01)	(0.00)			
Hytibar	0.1 b	0.1 a	0.3 a	0.1 b	0.1 a	0.2 a	0.005 b	0 a	0 a			
	(0.26)	(0.23)	(0.51)	(0.29)	(0.29)	(0.42)	(1.00)	(0)	(0)			

[a] Values for each fumigant within each variable followed by different letters are significantly different ($\alpha = 0.05$). Values in parentheses are the proportion of the total volatilization represented by the emissions from each bed dimension.

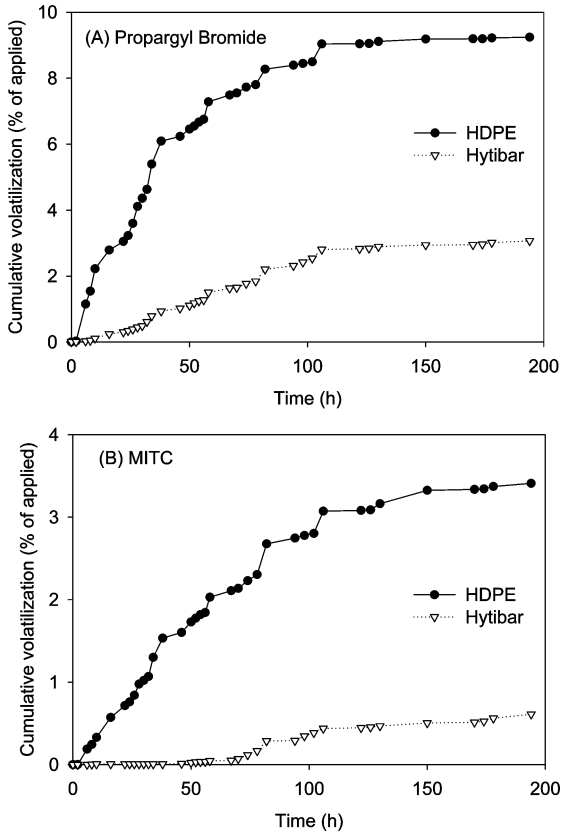

FIGURE 8. Cumulative emissions (% of applied) of (A) propargyl bromide and (B) MITC in the sand mesocosm experiment.

beds tarped with HDPE (Table 5). As observed for 1,3-D, emissions from the furrow (expressed as a % of the applied fumigant) were the same in both HDPE and Hytibar treatments, but very low emissions from the portions of the bed tarped with Hytibar resulted in nearly all the flux (87%) occurring from the untarped furrows (Table 5).

MITC. Tarping the bed with Hytibar was effective at reducing MITC emissions. Cumulative emissions of MITC from Hytibar-tarped beds were ~20% or less than those from HDPE-tarped beds (Table 2). Flux of MITC occurred at lower intensity for a longer period of time compared to 1,3-D and PrBr. Rapid flux of 1,3-D and PrBr occurring shortly after application resulted in a rapid increase in cumulative emissions (Figure 8A). In contrast, cumulative emissions of MITC increased more gradually (Figure 8B) due to the prolonged lower-intensity flux. For both surface tarps, maximum flux of 1,3-D and PrBr occurred before that of MITC. Thus, the proportion of the total flux occurring in the first 40 h after application from HDPE-tarped beds was greater for 1,3-D and PrBr (≥60%) than for MITC (~50%, Table 4). Emissions long after application (≥100 h) accounted for ~17% of the total measured MITC emissions from HDPE-tarped beds, but only ~10% of the total 1,3-D and PrBr emissions (Figure 8). Prolonged flux of MITC, continuing for >100 h after application, has also been observed in laboratory and field experiments (*7*, *11*, *22*).

Flux of MITC from the tarped portions of HDPE-covered beds (top plus side slope) accounted for >80% of the total emissions (Table 5). In the sand mesocosms, flux from the furrow of Hytibar-tarped beds was ~60% of the total, much lower than that for 1,3-D and PrBr (~90%) (Table 5). In the field study, MITC flux from the furrow was not measurable (Table 5). As discussed previously, transport of MITC was largely restricted to the tarped portions of the bed, thus limiting emissions from the furrow.

In both the sand mesocosm and field experiment, cumulative emissions of all fumigants tended to be greater for HDPE than for Hytibar (Table 2). This trend results from the lower permeability of Hytibar to fumigant vapors and has been observed in previous experiments (*12*−*13*). The sand in the mesocosms is coarse-textured and is expected to have low microbial activity. Thus, diffusion is rapid and transformation is slow in the mesocosm experiments compared to the field experiments and more fumigant volatilization was observed in the sand mesocosms (Tables 2−5). In addition, the cool, damp conditions during the field study may have further suppressed emissions compared to those from the sand mesocosm study: the mean air temperature was slightly cooler during the field experiment (11.6 vs 14.5 °C), and the mean relative humidity was significantly higher (70 vs 47%).

In these experiments, cumulative emissions of subsurface drip-applied 1,3-D, MITC, and PrBr in tarped bedded systems was relatively low, amounting to <10% of the applied mass. These experiments occurred under relatively cool conditions, with average air temperatures of 12−15 °C. A large fraction of the 1,3-D and PrBr flux was from the untarped furrows in beds tarped with VIF, indicating the importance of employing a means of decreasing emissions from the furrows in bedded systems to minimize total volatilization, especially under warm conditions when high flux is anticipated.

Because a 1-mil HDPE tarp does not achieve large reductions in emissions under most circumstances, alternative management practices (for example, use of a less permeable tarp or sealing the surface with water) must be used to minimize emissions of fumigant compounds. In both experiments, MITC showed a larger reduction in cumulative emissions with use of a VIF than 1,3-D and PrBr did (Table 2). This is due to the impacts of degradation and transport in the soil on fumigant emissions. Low concentrations of MITC can be rapidly transformed in soil (*23*). Fumigants that are rapidly transformed in soil show a stronger response to diffusion barriers because the increased residence time in soil results in a more substantial decrease in soil concentrations through degradation, leaving less fumigant available for volatilization. Transport of MITC in soil was more restricted than that of 1,3-D and PrBr (Figures 2 and 5). Low MITC concentrations in the furrow resulted in very low flux of MITC from the furrows, which was negligible in the field experiment (Table 5). Because a large fraction of 1,3-D and PrBr emissions came from the untarped furrows (Table 5), tarping the bed only with VIF was less effective for those compounds than for MITC.

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