Effect of Sequential Surface Irrigations on Field-Scale Emissions of 1,3-Dichloropropene

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A field experiment was conducted to measure subsurface movement and volatilization of 1,3-dichloropropene (1,3-D) after shank injection to an agricultural soil. The goal of this study was to evaluate the effect of sprinkler irrigation on the emissions of 1,3-D to the atmosphere and is based on recent research that has shown that saturating the soil pore space reduces gas-phase diffusion and leads to reduced volatilization rates. Aerodynamic, integrated horizontal flux, and theoretical profile shape methods were used to estimate fumigant volatilization rates and total emission losses. These methods provide estimates of the volatilization rate based on measurements of wind speed, temperature, and 1,3-D concentration in the atmosphere. The volatilization rate was measured continuously for 16 days, and the daily peak volatilization rates for the three methods ranged from 18 to 60 μg m^{-2} s^{-1}. The total 1,3-D mass entering the atmosphere was approximately 44−68 kg ha^{-1}, or 10−15% of the applied active ingredient. This represents approximately 30−50% reduction in the total emission losses compared to conventional fumigant applications in field and field-plot studies. Significant reduction in volatilization of 1,3-D was observed when five surface irrigations were applied to the field, one immediately after fumigation followed by daily irrigations.

Introduction

Ground-level ozone is a primary ingredient of photochemical smog and is a significant pollution problem in California. Ozone is formed in the troposphere by the reaction of volatile organic chemicals (VOC) and nitrogen oxides NO_x in the atmosphere and occurs predominately during the warm and sunny conditions of summer.

Recently, the U.S. EPA has established a new 8-h ozone standard, has identified regions throughout the country that are out of compliance, and is requiring state regulators to develop and submit plans to lower ground-level ozone to acceptable levels. Initial data from state regulators indicate the need to reduce emissions from many sources, including pesticides. Although, in general, pesticide VOC emissions are believed to be less than 3% of the total emissions statewide, in some agricultural areas such as the San Joaquin and Sacramento Valleys, pesticide emissions may contribute as much as 10%.

The state regulatory agencies' current VOC inventories are based on assuming that 100% of the VOC portion of an applied pesticide is lost to the atmosphere. This tends to overestimate the VOC loading, since pesticides are affected to some degree by irreversible sorption and abiotic and biotic degradation, which tend to reduce emissions. While assuming 100% emission may be convenient, this approach is not a suitable substitute for actual emission measurements under field-relevant conditions.

Regulations will be placed on activities that produce ozone as new, stricter rules governing ambient ozone levels are implemented. VOC emissions from soil fumigation will likely be considered in regions with significant agricultural production. Therefore, research is needed to accurately determine the true level of VOC emissions from soil fumigation and to develop methods to reduce emissions to low levels. Failure to do so may cause agricultural producers to face potentially restrictive control strategies, which may cause a reduction in profit or force growers to cease food production.

For soil fumigants, volatilization and degradation are two of the most important routes of dissipation (*1*−*3*). A large number of methods have been developed to reduce volatilization from soil and include the use of agricultural films (*4, 5*), soil amendments (*6, 7*), and application of water (*8, 9*), among many others. In arid regions, irrigation is commonly used to provide water needed for crop growth. Application of water to soils also reduces the available gas-phase porosity, reduces gas diffusion, and reduces volatilization (*10*). Therefore, irrigation offers a relatively simple and inexpensive method to reduce fumigant emissions.

A field experiment was conducted to measure the volatilization rate of 1,3-dichloropropene (1,3-D) after shank injection. 1,3-D has relatively high volatility and water solubility and relatively short field half-life (*11*). After fumigation, residual 1,3-D may be detectable in soil for several weeks. There have been few published field experiments describing efforts to measure field-scale emissions of 1,3-D after shank injection or for situations where irrigation water is applied shortly after application. The experimental data reported from this study provides state regulators and the scientific community with important information on emissions from soils.

Experimental Section

The field site was located in an agricultural production field near Buttonwillow, CA. The soil type was a Milham sandy loam and is classified as a fine-loamy, mixed, thermic Typic Haplargids. The upper 10 cm of soil in this series generally has from 0.5 to 1% organic matter, and rapidly falls to near zero levels below this depth.

The field experiment began on August 31, 2005, and was concluded September 16, 2005. About 2 weeks before conducting the field experiment, the soil was plowed followed by multiple disking operations to break up large soil aggregates. In addition, the field was sprinkler-irrigated and allowed to drain so that the initial soil−water content was approximately 0.2 cm^3 cm^{-3}. At the time of application, 1,3-D was applied to the field by a commercial applicator using a

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tractor containing nine shanks mounted on a 450 cm tool bar at 50 cm spacing increments. The target depth of application was 46 cm (i.e., 18 in.). Telone II (CAS Reg. No. 542-75-6) was applied to the field as a 97.5% mixture of 1,3-dichloropropene cis (CAS Reg. No. 10061-01-5) and trans (CAS Reg. No. 10061-02-6) isomers and 2.5% inert components. The application rate was 132 kg/ha (i.e., 12 gal/ac) and was applied to a nearly square area (178 m × 188 m) that equaled 3.4 ha (i.e., 8.4 acres). This results in a total applied mass of 447 kg.

The soil surface was irrigated with a total of 7.48 cm of water. The irrigation schedule was 1.88 cm of water applied immediately after fumigant application and 1.4 ± 0.13 cm of water applied each day for the following 4 days. After the fifth irrigation, the soil was allowed to dry.

In Milham sandy loam, 1,3-D has a reported soil degradation half-life of approximately 5 d (*9*). 1,3-D has a dimensionless Henry's law constant (K_h) of 0.04−0.06 (*12*) and an organic carbon distribution coefficient (K_{oc}) of 32 $cm^3\ g^{-1}$ (*11*).

Measurements of 1,3-D in Air. The concentration of 1,3-D in atmosphere was obtained by passing air through charcoal sampling tubes (SKC 226-09, SKC, Inc., Fullerton, CA). The charcoal tubes contained two beds, 400 and 200 mg, of coconut charcoal. A vacuum system was used to draw air through the charcoal sampling tube at a nominal flow rate of 150 $cm^{-3}\ min^{-1}$. After each sampling interval, the tubes were removed from the sampling mast, capped, stored on ice, and transported to a freezer for temporary storage. Several times during the experiment, the samples were removed from the portable freezer, placed in an ice chest, transported to the laboratory, and stored in a freezer until analysis of the 1,3-D concentration. Chemical breakthrough tests for the charcoal sampling tubes were conducted in the laboratory prior to the field experiment to verify that the second charcoal bed was free of 1,3-D.

Samples of the 1,3-D concentration in the soil pore space were taken at four locations in the field (see Supporting Information) using stainless steel samplers installed at 15, 30, 45, 60, 75 and 100 cm depths. A gastight syringe was used to draw 50 cm^3 of the soil pore air space through charcoal sampling tubes, trapping the 1,3-D. At later times, 500 cm^3 of soil air space was sampled to ensure sufficient 1,3-D mass was collected on the sorbent for analysis.

Since the primary method to obtain the volatilization rate involved the use of micrometeorological methods, the field site was located in a production area with large vacant field areas that provided large up-wind distances between the instruments and the treated field boundaries. Atmospheric and soil measurements of the 1,3-D concentration were collected for a 16-day period over the center of the field. The concentration of 1,3-D in the atmosphere was collected at 10, 40, 80, 159, 236, and 360 cm above the soil surface. During the first 6 days of the experiment, the measurement periods consisted of 2-h samples from 0700−2100 h and a 10-h nighttime sample. Beginning on the day 7, there were 3-h sample intervals from 0700−1900 and a 12-h nighttime sample. Beginning on the day 10, two 6-h daytime and a 12-h nighttime sample were collected. Beginning on day 13, two 12-h samples were collected each day. Measurements of the 1,3-D concentration at several locations surrounding the field and 1.5 m above the land surface were also collected using this sampling schedule. Longer sampling periods were used later in the experiment to ensure sufficient mass was collected in the sampling tubes, since volatility losses for 1,3-D typically decrease over time.

Various meteorological measurements were also obtained, including incoming radiation, net radiation, air temperature, wind speed, wind direction, and relative humidity. Meteorological information is necessary to determine the volatilization rate using the aerodynamic (ADM) (*13*), integrated horizontal flux (IHF) (*14*), and the theoretical profile shape (TPS) (*15*) methods.

Chemical Analysis. A charcoal sampling tube was removed from the freezer and warmed to room temperature. The tube was cut, each charcoal bed was transferred to a 10 cm^3 headspace vial, and 3 cm^3 of acetone was added to the vial, which was immediately sealed with an aluminum cap with Teflon-lined septum. Then, the vial was vigorously shaken for 30 min in a reciprocating shaker. Afterward, 1 cm^3 of the acetone supernatant was transferred into a 2 cm^3 GC vial and immediately capped. The GC vial was then stored at −70 °C until GC analysis.

The 1,3-D analysis was conducted using an Agilent 6890 series gas chromatograph (Agilent Technologies, Palo Alto, CA) with a microelectron capture detector (μECD). The column used for the analysis was a 30 m × 0.025 cm DB-VRX column. The inlet temperature was set at 240 °C and detector temperature at 290 °C. A temperature program was used that included the following sequence: keeping initial temperature at 50 °C for 1 min, increasing to 80 °C at 4.0 °C/min and remaining for 2 min, and then increasing from 80 to 120 ° C at 30 °C/min and remaining for 2 min. The injection volume was 2.0 μL and the split ratio was 20:1. The makeup gas was nitrogen with a flow rate of 60 cm^3/min.

The limit of detection (LOD) and the limit of quantification (LOQ) of this method were 0.015 and 0.05 μg/tube, respectively. Repeated tests were conducted at 1, 5, 10, and 1810 times the LOQ to determine the recovery of 1,3-D vapors trapped by charcoal sampling tubes at a airflow rate of 150 cm^3/min, for both very low and very high concentrations. The recovery was found to be 84 ± 7% (*cis*-1,3-D) and 86 ± 7% (*trans*-1,3-D). Further, by connecting four sampling tubes in series and sampling for 8 h, it was found that more than 99.99% of the total mass was contained in the first tube.

Meteorological Measurements. Wind speed measurements were obtained using five Thornthwaite anemometers (CWT-1806, C.W. Thornthwaite Assoc.) positioned at 20, 40, 80, 160, and 240 cm above the field surface. In addition, a MetOne (014A, Campbell Scientific Inc.) wind speed sensor was placed at 344 cm. The air temperature gradient was obtained by placing pairs of fine-wire thermocouples (FW3, Campbell Scientific, Inc.) at 40 and 80 cm heights and connecting them to a data logger (10X, Campbell Scientific, Inc.) in a configuration that allows the gradient to be measured directly. Other meteorological information was also obtained, including relative humidity and temperature (HMP35C, Campbell Scientific, Inc.), incoming solar radiation (LI-200S, LI-COR, Inc.), net solar radiation (Q-6, Radiation and Energy Balance Systems, Inc.), and barometric pressure (Vaisala PTA-427, Campbell Scientific, Inc.). The field layout showing position of the sensors is shown in the Supporting Information.

Methods for Measuring the Volatilization Rate. The 1,3-D volatilization rate was obtained using three methods: aerodynamic, integrated horizontal flux, and theoretical profiles shape methods. A volatilization rate obtained using the aerodynamic method (ADM) is based on gradients of wind speed, temperature, and 1,3-D concentration (*13*) collected over a relatively large and spatially uniform source area. Since there is an abrupt change in the surface condition at the boundary of the treated area, the instruments need to be placed at a height where the atmospheric conditions near the surface have reached a quasiequilibrium (i.e., the gradients are fully adjusted). Using wind tunnel experiments, this height has been found to be approximately 1−2% of the upwind distance between the sampling instruments and the edge of the treated soil (*16*). For the tested field, 1% of the smallest possible upwind distance indicates that the instruments should be placed below a 90 cm height. The integrated

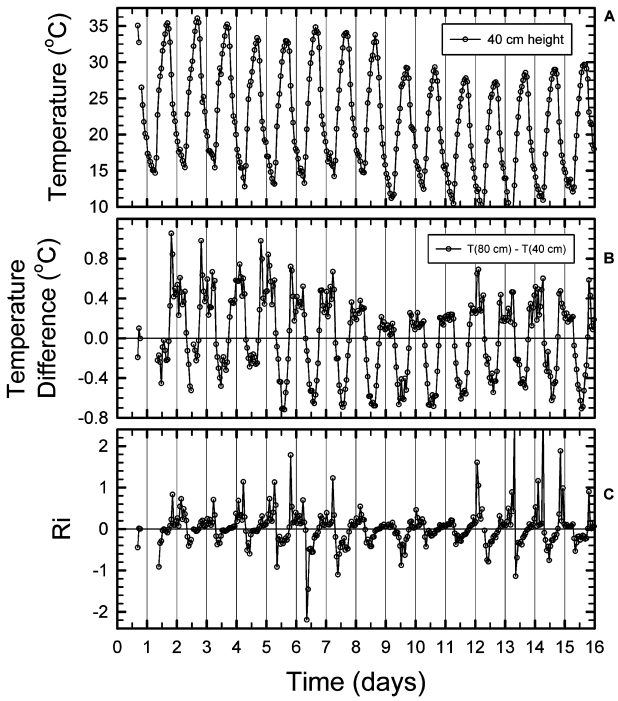

FIGURE 1. Air temperature (°C) at 40 cm height above the soil surface (A), temperature difference between 80 and 40 cm heights (B), and gradient Richardson's number (C). Integer values on the time axis indicate midnight.

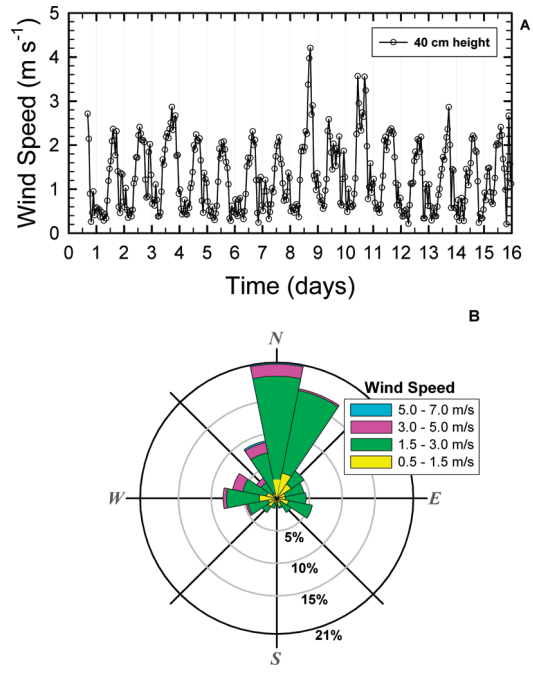

FIGURE 2. The variation in wind speed (m s^{-1}) at 40 cm above the soil surface during the experiment (A). A wind rose diagram (B) showing the wind direction, speed, and probability the wind will occur in a specific direction.

horizontal (IHF) flux method (*14*) uses concentration and horizontal wind speeds measured at several heights. The flux is determined using principals of mass balance where the 1,3-D mass leaving the soil surface upwind from a sampling point is presumed equal to the mass that passes through a vertical plane located at the sampling point. Using a mass balance approach has an advantage in that no correction for atmospheric stability is needed. The theoretical profile shape (TPS) method (*15*) is based on the trajectory simulation model of Wilson et al. (*17*) and allows the 1,3-D volatilization rate to be obtained from a measurement of concentration and wind speed at a single height above the soil surface. The method does not require large up-wind distances and is relatively insensitive to the atmospheric stability, so temperature and wind gradients and stability corrections are unnecessary. See Supporting Information for additional details.

Results and Discussion

Ambient Conditions. Figure 1 shows the ambient temperature at a 40 cm height above the soil surface during the 16-day experiment, and integer values on the time axis indicate midnight. Measurements of the global irradiance (W m^{-2}), net solar radiation (W m^{-2}), and relative humidity (%) are shown in Figure S-2 (Supporting Information) and provide information on available energy at the surface to heat the soil, heat the atmosphere, and induce evaporation. The weather pattern during the experiment included hot temperatures and clear-sky conditions. Soil and ambient temperatures are affected by net solar radiation, so it is not surprising that the temperature pattern is fairly smooth. During the first 8 days of the experiment, the maximum temperature was approximately 35.7 °C, daily minimum temperature was 13.2 °C, and the averaged temperature was 23.8 °C. After day 9, cooler temperatures were observed with daily highs of approximately 28.8 °C, lows of approximately 9.6 °C, and an average of 19.1 °C.

Parts B and C of Figure 1 are graphs of the temperature gradient and the gradient Richardson number during the experiment. The temperature gradient was obtained from measurements taken at 80 and 40 cm above the soil surface, and a negative value means that the temperature near the surface was greater than the temperature at positions higher in the atmosphere. The gradient Richardson number is a dimensionless parameter describing the relative importance of buoyancy and convective forces and approaches zero for neutral stability conditions. By definition, the sign of the Richardson number is determined by the temperature gradient.

In general, the temperature gradient varied ±1 °C and the Richardson number varied by ±2 throughout the experiment, and negative values, indicating unstable conditions, generally occurred during the middle of the day. Unstable conditions generally leads to increased volatilization, since the air over the soil surface is buoyant compared to the air above and rises. Buoyancy-driven convection can transport the fumigant away from the soil surface and increases the concentration gradients across the soil−atmosphere boundary, which is an important driving force in the volatilization process.

The presence of the irrigation water at the beginning of the experiment led to reduced daytime temperature differences, as shown by smaller midday negative values (Figure 1B). During the irrigation period, the average temperature difference between the hours of 1100 and 1300 was −0.24 °C. Later in the experiment, the average temperature difference between 1100 and 1300 was −0.54 °C.

The wind speed at a height 40 cm and wind direction at a height of 1000 cm are shown in Figure 2. The winds are predominately out of the north, as shown in the wind rose diagram (Figure 2B). The maximum wind speed was 4.2 m/s, but daily maxima were generally from 2 m/s to a high of about 3 m/s. During the middle of the night, wind speeds were commonly from 0.2 to 0.4 m/s.

Air Concentrations. Concentrations of 1,3-D in the atmosphere were collected in the center of the field. The concentrations at 40 and 80 cm above the surface are shown in Figure 3. The levels were relatively high during the first 4 days of the experiment and were very low after 8 days.

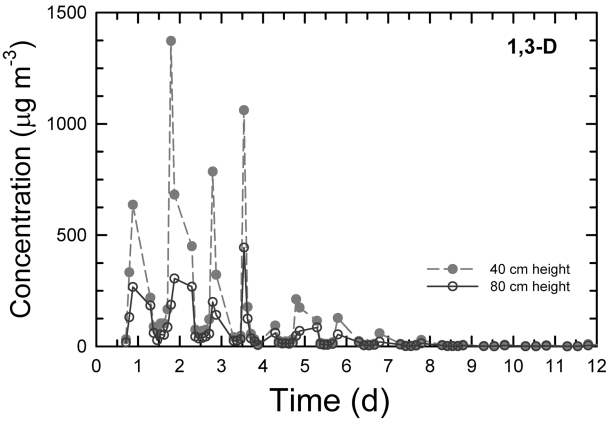

FIGURE 3. Measured 1,3-D concentration (μg m^{-3}) in the atmosphere at 40 and 80 cm above the soil surface.

Observed concentrations at a height of 40 cm exceeded 1000 μg m^{-3}, while at a height of 80 cm the concentration remained below 500 μg m^{-3}. These levels are significantly higher than the concentrations measured at eight locations surrounding the field (data not shown). For example, the peak measured concentration located at the field center at a height of 159 cm was 137 μg m^{-3} and occurred during the 24th sample period (i.e., at 3.58 d). At the same time, the peak measured concentration 3000 cm outside the field boundary, at a height of 150 cm, was 6.12 μg m^{-3}.

The large concentrations at the beginning of the experiment were due primarily to the larger soil fumigant mass present in the soil shortly after application and the rapid soil diffusion caused by the presence of soil disturbances resulting from the fumigation shanks (*18*). As the fumigant volatilizes and degrades, atmospheric concentrations are reduced. The presence of the irrigation water also plays a role in the 1,3-D concentration in the atmosphere. While increased water content at the soil surface tends to reduce gas-phase diffusion to the atmosphere by reducing the air phase porosity (*10*), higher water contents at the surface increase evaporative cooling, which tends to create more stable atmospheric conditions when compared to the presence of a hot and dry surface. For a similar volatilization rate, this will lead to higher atmospheric concentrations. The cooling effect of applying irrigation water to the soil surface is readily seen in Figure 1B, with smaller temperature differences shortly after irrigation. This effect is also apparent in the values of the gradient Richardson number, which tend toward zero shortly after irrigation, and this pattern continues until the soil is allowed to dry, after day 5. Under stable conditions (e.g., positive Richardson number), the air mass over the field experiences less vertical mixing, which leads to increased concentrations. The increased concentration in the atmosphere also reduces the concentration gradients across the soil−atmospheric boundary. This can lead to a reduction in volatilization relative to more unstable conditions.

1,3-D Volatilization. Shown in Figure 4 are time series of the volatilization rate (i.e., flux density) and the timing and amounts of irrigation water applied to the field. The three methods demonstrate a similar temporal pattern throughout the experiment. Under nonirrigated conditions, peak fumigant volatilization rates commonly occur during the midday (*3, 19, 20*). However, application of surface irrigation causes the midday peak volatilization rates to be damped by the apparent formation of a surface water seal. The surface water seal inhibits fumigant transport to the soil surface by reducing, or eliminating, the gas-phase diffusion process by filling the soil pore space with water or by 1,3-D partitioning into the water phase. For this soil, the porosity was approximately 0.5 cm^3 cm^{-3}, soil liquid-phase diffusion coefficient was 0.0078 cm^2 d^{-1}, and the soil gas-phase diffusion

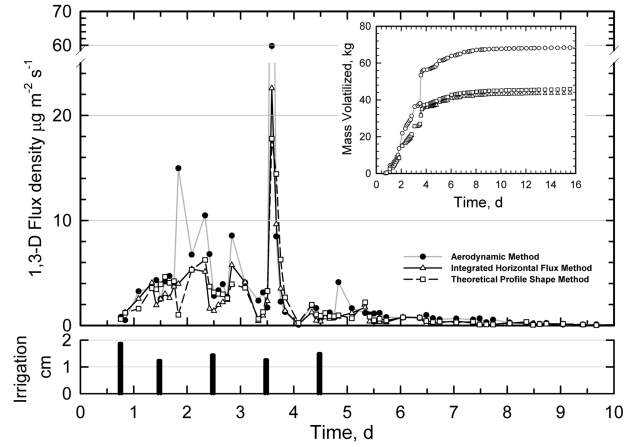

FIGURE 4. Volatilization rate (μg m^{-2} s^{-1}) and timing and amount of irrigation water as a function of time (d) after application for the aerodynamic (solid line, circles), integrated horizontal flux (solid line, triangles), theoretical profile shape methods (dashed line, squares). The inset shows cumulative 1,3-D emission as a function of time after application.

coefficient was 1100 cm^2 d^{-1}. Fumigant diffusion through a soil saturated with water is approximately 5 orders of magnitude less than diffusion through the same soil at 25% of saturation; clearly, soil gas diffusion dominates when the soil pores are devoid of water.

The maximum daily volatilization rate for each method occurred on the third day (t = 3.54 d) and ranged from approximately 18 to 60 μg m^{-2} s^{-1}. Upon viewing Figure 4, it is clear that, for several measurement periods, the ADM estimates higher volatilization rates compared to the IHF and TPS methods and that the IHF and TPS methods agreed more closely throughout the experiment.

The inset shown in Figure 4 provides an illustration of the total 1,3-D mass lost to the atmosphere with time after application. This information was obtained by integrating the volatilization rate over time and multiplying by the total field area. It is clear that the IHF and TPS methods provide estimated volatilization rates that were very similar. After 16 d, the total emission estimates from the IHF and TPS methods were between 9.8 and 10.3% of the applied material. The cumulative emission estimate from the ADM, however, is larger and after 16 d was determined to be 15.3%. On the basis of the amount of 1,3-D applied to the field, the ADM estimate is 5.2% greater mass loss than the IHF and TPS methods. The average total mass lost for the three methods was 11.8%, with a standard deviation of 3%. These results are consistent with estimates of the experimental uncertainty for emissions of methyl bromide obtained using the ADM, as reported by Majewski (*20*), which was based on a regression analysis of the log−linear wind speeds and concentrations with respect to height. This analysis should also apply to other fumigants that have log−linear concentration profiles. In a report by Wilson and Shum (*21*), the theoretical accuracy of the IHF method was determined using a Lagrangian stochastic model and found to be within approximately 20% for appropriately large field sites and surface roughness lengths below 10 cm. This study also provides guidelines that can be used to design IHF experiments with suitable experimental accuracy.

It is clear from Figure 4 that, for most of the experiment, the measured ADM flux rates were similar in magnitude to the IHF and TPS methods. However, for a few time periods the ADM flux is considerably larger than the IHF and TPS methods. To investigate the relative effect of these values, their contribution to the total emissions was determined. The single largest value occurred at t = 3.54 d and the difference between the ADM and IHF-TPS methods represents 2.3% of the cumulative emissions and explains 43% of the difference between methods on a

TABLE 1. Total Emissions (kg) of 1,3-D[a]

method	*cis*-1,3-D	*trans*-1,3-D	1,3-D
aerodynamic	39.1 (17.5)	29.3 (13.1)	68.4 (15.3)
integrated horizontal flux	25.8 (11.5)	18.1 (8.1)	43.9 (9.8)
theoretical profile shape	27.0 (12.1)	19.3 (8.6)	46.2 (10.3)

[a] Numbers in parentheses are percent of applied. The total 1,3-D mass applied was 447 kg.

percent-difference basis. The effect of the five points with the largest differences was found to contribute 3.5% to the cumulative emissions and explains 66% of the percent difference between the methodologies. Although this analysis suggests that the ADM overestimated the cumulative emissions, no quantitative information is available on an absolute scale to determine if one or more methods overestimated or underestimated the flux rates.

A laboratory study quantifying 1,3-D flux loss was conducted using soil collected from the field site for comparative purposes (*9*). The study was conducted with temperatures cycles that closely matched field observations. This study reported that the total emissions of *cis*-1,3-D after 14 days were 33.1% for a nonirrigated treatment and 17.1% for an irrigation treatment that duplicated the amounts and timing of water applied to the field. The laboratory results compared very well with the estimated total *cis*-1,3-D emission (Table 1) using the aerodynamic method (i.e., 17.5%) but is larger than the total *cis*-1,3-D field emissions estimates from the TPS and IHF methods (i.e., 11.5−12.1%).

Another study of 1,3-D volatilization from a large field in the Salinas Valley of California reported that 25% of the applied material was lost to the atmosphere (*22*−*24*) over a 14-day sampling period. The ADM was used to estimate the volatilization rate and the total emissions. During this experiment, irrigation water was not applied to the field and, therefore, also suggests that repeated surface irrigation could reduce emissions by as much as 30−40%.

Gao et al. (*25*) conducted a field plot experiment to investigate several methods to reduce emissions of 1,3-D after shank injection. The experiment was conducted in a Hanford sandy loam and included a 46 cm injection depth. Emissions were periodically measured using passive flux chambers, and total emissions from a bare-soil, nonirrigated control were 36% of the applied 1,3-D, which is similar to the value obtained in the laboratory experiment of Ashworth and Yates (*9*). While this study did not include a postfumigation sequential irrigation treatment, they studied the effect of applying water prior to soil fumigation and found that this could reduce emissions by nearly 50%.

Soil Gas-Phase Concentration. Shown in Figure 5 is the soil gas-phase concentration at various times after application of 1,3-D. After 24 h, the soil gas-phase concentration for 1,3-D at the injection depth exceeded 2.5×10^7 μg m^{-3}, and the treated zone had extended from about 30 to 70 cm depth. Each day, the concentrations in soil were reduced as diffusion moved 1,3-D throughout the soil. By day 4, a fairly constant concentration was observed from 20 to 80 cm depth. By day 11, soil concentrations were low along with the volatilization rate (see Figure 4).

Summary

The results of this study indicate that applying sprinkler irrigation water to the soil surface following soil fumigation leads to total 1,3-D emissions between 10 and 15% of the applied material. On the basis of recent laboratory and field

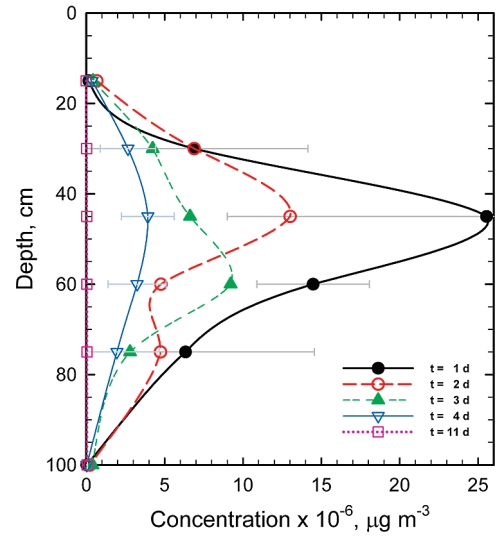

FIGURE 5. Soil gas phase concentration (μg m^{-3}) with depth (cm) in soil. Each line represents the concentration distribution at a particular time after application. Error bars are provided on two curves (t = 1 and 4 d) to give an indication of the variability of the soil gas concentration across the four sampling locations.

experiments conducted under similar soil and environmental conditions, it appears that atmospheric emissions of 1,3-D can be reduced by 30−50% compared to conventional application methods. This provides a simple, effective, and low-cost method to protect the environment from agricultural chemicals and to reduce VOC emissions to the atmosphere. This study also demonstrates that 1,3-D and, hence, VOC emissions from field soil are significantly less than current regulatory estimates.

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Supporting Information Available

A description of the meteorological methods used in this study, a schematic of the field site, global irradiance, net radiation, relative humidity, soil−water content, and bulk density data. This information is available free of charge via the Internet at http://pubs.acs.org.

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