1,3-Dichloropropene and Chloropicrin Emissions Following Simulated Drip Irrigation to Raised Beds under Plastic Films

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Using laboratory soil chambers a nonscaled representation of an agricultural raised bed was constructed. For a sandy loam soil, 1,3-dichloropropene (1,3-D) and chloropicrin (CP) were applied at 5 cm depth with an excess of water (simulated drip irrigation). Application was made under both high density polyethylene (HDPE) and virtually impermeable film (VIF) covering the soil bed (the furrow was left uncovered). Soil gas distribution of the fumigants, together with emissions into the headspace above the bed, sidewall and furrow were determined over time. Total emissions from the HDPE treatment were cis 1,3-D 28%, trans 1,3-D 24%, and CP 8%. Due to its lower permeability, the values for VIF were 13%, 7%, and 1.5%, respectively. With HDPE, the majority (86–93%) of the emissions occurred from the bed, while for VIF the majority (92-99%) of the emissions was from the furrow. Compared to a range of literature values for shank injection, the use of drip application appears to offer a benefit in reducing 1,3-D and CP emissions. However, the most meaningful comparison is with our previous data for simulated shank injection where the same soil was covered (completely) with the same plastic films (1). In this comparison, only 1,3-D emissions under HDPE were lower with drip application; 1,3-D emissions under VIF and CP emissions under both films were greater with the drip application.

Introduction

Reducing the soil-to-air emission of agricultural fumigants is increasingly important to protect both human and environmental health. The high vapor pressure of preplant fumigants such as 1,3-dichloropropene (1,3-D) and chloropicrin (CP) (Table 1) renders them liable to transfer from the soil and thereby adversely affect air quality. The presence of the fumigants in air, together with their role in the formation of near-surface ozone (smog) are two areas of particular concern. Therefore, research is focusing on approaches that reduce emissions either by application strategy (e.g., reducing amounts of applied chemicals, differing application type) or by postapplication strategy (e.g., plastic film covering, water sealing, surface amendment).

One approach to potentially reduce emissions of fumigants is the use a subsurface drip application under plastic film. This reduction is based on the degree of solubility and relatively low Henry's constants of fumigants such as 1,3-D and CP (Table 1). For example, compared to fumigants such

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as methyl bromide and methyl iodide, 1,3-D and CP have a lesser propensity to partition into the gaseous soil phase. In contrast to shank injection therefore, where the predominant mechanism of fumigant movement is vapor diffusion, drip applied 1,3-D and CP are likely to be initially transported with the irrigation water downward and laterally into the soil. Under such conditions, the presence of the fumigants in the water phase, the increased path length to the soil surface, and the increase in soil moisture content all serve to potentially lower emissions. It has been suggested (2) that drip application of soluble formulations may ensure a more uniform distribution of fumigants in the soil, and is likely to reduce emissions, worker exposure, and the amount of chemicals applied relative to conventional shank application. For example, comparison of a 46 cm shank injection to a 20 cm drip application for both 1,3-D and CP (3) showed that under HDPE, 1,3-D emissions were reduced from 43% with shank injection to 12% with drip application, and CP emissions were reduced from 17% (shank) to 2% (drip). A high level of uniformity in the distribution of drip-applied fumigants within the soil is also likely to improve pest control. This may be particularly important for fumigants with relatively low vapor pressures (e.g., compared to methyl bromide and, to a lesser extent methyl iodide) where extensive gas phase diffusion away from the point of application may not be apparent. Indeed, gas phase distribution was markedly improved by drip application when compared to shank injection (2).

Nevertheless, shank injection of 1,3-D and chloropicrin typically takes place at 30 or 46 cm depth, whereas drip application usually takes place at, or just below, the soil surface. Therefore, any potential benefit in emissions reduction offered by the irrigation water may be offset by the closeness of the application to the soil surface. For example, if the irrigation water is inefficient in transporting the fumigant to greater soil depth, high emissions may occur due to a short soil-to-atmosphere path length. This can be somewhat mitigated by the presence of plastic film over the bed surface since this acts as a barrier at the soil-atmosphere interface. The rate of gas diffusion across this barrier is then controlled by the permeability of the film to a specific fumigant. High density polyethylene (HDPE) is the standard film used in such operations but has been frequently noted to offer poor impermeability to fumigants such as 1,3-D and CP (4-6). However, plastics with lower permeability, for example, virtually impermeable film (VIF), although more expensive, can offer dramatic reductions in the emissions of such fumigants. By maintaining fumigants in the soil, such films increase pesticidal efficacy by increasing fumigantpest contact time (i.e., concentration × time index) and can ultimately lead to the chemical/biological degradation of the fumigant within the soil.

Often, 1,3-D and CP are applied together to provide a synergistic effect in relation to pest kill. Although 1,3-D is very effective as a nematicide and herbicide, its relatively poor fungicidal efficacy is compensated for by the CP (7). As the commercial product "Inline" (Dow Agrosciences) the two chemicals (approximately 65:35 1,3-D:CP) are commonly used in combination for drip application situations (e.g., raised bed agriculture). Using laboratory soil columns, the aim of the work described in this paper was to approximate a drip application (i.e., fumigant application with an excess of water to transport the fumigant throughout the soil bed) of 1,3-D and CP to raised beds under both HDPE and VIF, and determine volatile fumigant emissions from the soil.

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TABLE 1. Selected Properties of cis 1,3-D, trans 1,3-D, and Chloropicrin

	solubility at 25 °C (mg L ⁻¹)	vapor pressure at 25 °C (mm Hg)	Henry's constant (dimensionless)
<i>cis</i> 1,3-D	2.18 ^a	34.3 ^a	0.056 ^c
trans 1,3-D	2.32 ^a	23.0 ^a	0.037 ^c
CP	2.00 ^b	23.8 ^b	0.103 ^c
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^{*a*} From Thomas et al. (*19*). ^{*b*} From California Department of Pesticide Regulations (*20*). ^{*c*} From Wang et al. (*18*).

Materials and Methods

The experiment was performed using purpose-built aluminum soil chambers that allowed for an actual size (nonscaled) construction of half-a-bed and half-a-furrow. The design of these chambers has been described in detail previously (\mathcal{B}), therefore only a brief description will be given here. Rectangular soil chambers (120 cm high ×80 cm wide ×10 cm deep) were packed with soil in such a way as to form half a bed (50 cm wide) and half a furrow (30 cm deep, 30 cm wide at its top and 25 cm wide at its base) across the width of the chamber. A field moist sandy loam soil from Buttonwillow, CA (thermic Typic Haplargids; Milham series) was packed into the chamber to a bulk density of 1.5 g cm⁻³. The surface layer of the soil had a pH of 7.9 and an organic matter content of around 2%. All treatments were performed in duplicate.

Either a 1 mil HDPE film (Dow Chemical Company, Midland, MI) or a 1.5 mil Hytibar VIF (Klerk's Plastics, Hoogstraten, Belgium) was sealed over the surface of the bed and sidewall (furrow base was left uncovered) and a volatilization chamber placed atop. In these chambers, it was possible to seal and isolate the headspace above the bed, sidewall, and furrow compartments and thus determine the contribution of each compartment to the overall emissions loss. The 1,3-D (as Telone II, 50:50 cis:trans isomers) and CP (both from Dow Agrosciences, Indianapolis, IN) were applied at a depth of 5 cm below the bed surface at twothirds distance from the bed shoulder. Application equated to field application rates of approximately 80 kg ha⁻¹ cis 1,3-D, 80 kg ha⁻¹ trans 1,3-D and 84 kg ha⁻¹ CP (based on bed surface area). These rates closely matched the ratio of 1,3-D to CP in the commercial drip application product Inline, (although in contrast to the commercial product, no surfactant was added to our system). Immediately following injection of the fumigants via a sealable port in the face of the chamber, 1 L water was applied through the same port at a rate of 8 mL min⁻¹. Thus, the application took place over a period of around 2 h. The relatively high solubility of both fumigants (Table 1) ensured the downward and lateral movement with the flow of irrigation water from the point of application. This procedure was used as a surrogate for a typical 2 h field drip-application of 1,3-D and CP using standard 0.67 gallon min⁻¹ 100 ft⁻¹ drip tape. Application was commenced at 11:00 h (Time 0).

The temperature of the surface soil was manipulated to approximate a diurnal regime typical of temperatures recorded at the Buttonwillow site during September 2007 (ranging from 23 to 32 °C at 5 cm depth). This was achieved by controlling the air temperature of the experimental room in which the chambers were housed. Below 30 cm depth, the outside of the chambers were insulated with foam to lessen temperature variation at depth. Sampling of fumigant emissions from the soil was carried out by pulling the headspace air through XAD-4 (2 section 400/200 mg) sorbent tubes (SKC Inc., Eighty Four, PA). Due to the large size of the volatilization chambers, a mass flow rate of 1 L min⁻¹ was used to sweep the headspace air, of which a subsample of XAD-4 tubes were stored at -19 °C until extraction and analysis. The tubes were extracted first by separating their two sections and placing each into 20 mL glass vial. After the addition of 4 mL of hexane, the vials were immediately capped with a Teflon-faced butyl rubber septum and aluminum crimp seal, shaken for 30 min, and around 1.5 mL of supernatant solution transferred to a glass vial for analysis. The two sections of the XAD-4 tubes were extracted and analyzed separately.

Analysis of XAD-4 extracts was carried out using an Agilent Technologies 7890C gas chromatograph (GC), equipped with a microelectron capture detector. The column was a DB-VRX 122-1534 with dimensions of 30 m × 250 μ M × 1.4 μ m (Agilent Technologies) running at a flow rate of 1.6 mL min⁻¹ and with He as the carrier gas. The inlet temperature was 240 °C and the detector temperature 290 °C. The GC oven temperature was maintained at 45 °C for 1 min after sample injection, increasing to 75 °C at a rate of 2.5 °C min⁻¹, and then to 140 °C at a rate of 35 °C min⁻¹ before being held at this temperature for 3 min. Under these conditions, retention times of *cis* 1,3-D, *trans* 1,3-D and CP were 10.4, 11.7, and 13.1 min, respectively. A set of 10 standards encompassing the range of *cis* and *trans* 1,3-D and CP concentrations of the samples were prepared in hexane.

Soil gas samples were analyzed using a Hewlett-Packard HP6890 GC coupled with a G1888 Network Headspace Sampler (Agilent Technologies). Similar GC conditions to those described above were used. The operating conditions for the headspace sampler were as follows: oven temperature 80 °C, loop temperature 90 °C, transfer line temperature 100 °C, vial equilibration time 5 min, and sample loop volume 0.2 mL. For all analyses, five standards, encompassing the range of *cis* and *trans* 1,3-D and CP concentrations observed in the samples were prepared in a small volume (1–5 μ L) of hexane.

Results

Flux rates (arithmetic means) of the fumigants from the HDPE and VIF treatments over the course of the experiment are shown in Figure 1a and b, respectively. These are the total fluxes, that is, from the bed, sidewall, and furrow combined. In general, the *cis* and *trans* isomers showed similar emission pattern, although, in most cases the rates for the *cis* isomer were higher. In each case, the 1,3-D isomers showed greater flux rates than the CP. However, this difference was least marked in the HDPE treatment where CP fluxes were comparable to those of *trans* 1,3-D. Fluxes of the 1,3-D isomers occurred over longer time periods than for CP. In general, CP emissions ceased after around 75 h under HDPE and around 150 h under VIF.

Comparing HDPE and VIF, it is noticeable that the HDPE led to a more rapid release of the fumigants causing an initial peak followed by extensive tailing over time. In the VIF treatment the, albeit lower, fluxes were spread over a longer period and had no obvious single emissions peak. Under HDPE, emission fluxes rapidly peaked before tailing off over time. The highest emission value was reached most rapidly for the *cis* 1,3-D isomer (14 h), followed by the *trans* and CP (both at 21 h). At these times, the mean flux rates were around 14.5 μ g m⁻² s⁻¹ for the *cis* isomer, around 10.5 μ g m⁻² s⁻¹ for the *trans* isomer, and around 10 μ g m⁻² s⁻¹ for CP. Under VIF, emission fluxes increased rapidly at the start of the

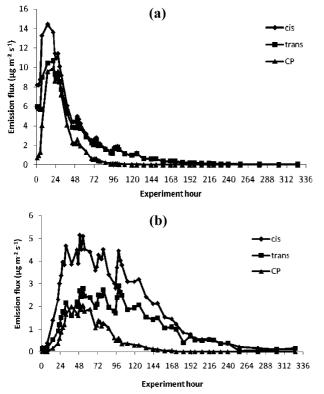


FIGURE 1. Arithmetic mean (n = 2) flux rates of each fumigant over the course of the experiment from the (a) HDPE and (b) VIF treatments. Application was carried out at 11:00 h (Time 0).

experiment but, overall, the emission curves were much broader than for HDPE. For the 1,3-D isomers, emissions were highest from around 25 to 100 h. For CP, emissions were highest from around 30 to 60 h. Highest emission rate for the *cis* isomer was $5.1 \,\mu g m^{-2} s^{-1}$ (at 53 h), for the *trans* isomer was $2.9 \,\mu g m^{-2} s^{-1}$ (at 99 h) and for CP was $2.1 \,\mu g m^{-2} s^{-1}$ (at 49 and 53 h).

When expressed as a percentage of the total amount of fumigant added to the system (Table 2) it is clear that in all cases CP emissions were lower than for the 1,3-D isomers. Moreover, Table 2 highlights differences between the plastic types. VIF dramatically reduced total emissions compared to HDPE. For example, for *cis* 1,3-D this reduction was 54%, for *trans* 1,3-D was 71%, and for CP was 81%. The distribution of emissions between the three compartments of the raised bed system is also shown in Table 2. Under HDPE the predominant emission loss for each fumigant was via the bed surface, that is, close to the point of application. However, under VIF, emissions occurred primarily via the furrow.

The distribution of *cis* 1,3-D at 24 h after injection under HDPE and VIF are shown in Figure 2a and b, respectively. The distribution of *trans* 1,3-D and CP were similar to the *cis* isomer and are not presented here. In the VIF chamber, the data show concentrations decreasing radially from the point of injection. In the HDPE chamber it is noticeable that the point of highest concentration was not at the point of injection and it is unclear why this should be the case. Nevertheless, a similar radial distribution from this point is observed. Gas phase concentration was generally higher under VIF, and the peak concentration was almost double that of the HDPE treatment. In both the VIF and HDPE treatments, a widespread distribution of the fumigants throughout the bed region was observed.

Discussion

In relation to risk assessment associated with fumigant use, the flux rate (a precursor of time course air concentrations) is an important consideration. High flux rates are of concern in terms of the health of agricultural workers and local populations, particularly during the initial period following fumigation when rates are usually highest. Clearly, the rapid, relatively high flux rates observed in the HDPE treatment demonstrate that this risk would be substantially greater when HDPE, rather than VIF, is used as a surface containment. The permeability of these films was tested previously (1) using a previously reported technique (5). Mass transfer coefficients at 20 °C (cm h^{-1}) were determined for HDPE as *cis* 2.0; *trans* 3.7, CP 0.6, and for VIF as *cis* 0.001; *trans* 0.002; CP 0.0002. Clearly, the higher emissions from the HDPE treatment were a result of the much greater permeability of this film to each fumigant. The lower CP mass transfer coefficients for both films are consistent with the lower emissions observed for this fumigant compared to 1,3-D. However, these lower emissions are also likely due to the difference in degradation rate, half-life, which was previously measured as 2.9 h for CP and 90 h for 1,3-D in this soil (1). Therefore, this more rapid degradation loss pathway for CP will have significantly reduced emission losses from the soil surface. In contrast, the relatively long half-life and higher mass transfer coefficients for cis and trans 1,3-D resulted in higher emissions. The higher vapor pressure for cis 1,3-D (Table 1) explains its greater emissions when compared to trans 1,3-D. In field experiments comparing the emissions of 1,3-D and CP from surface drip-application under both HDPE and VIF (9) a similar extent of emission reduction due to VIF use was observed.

Tarp type also had a strong effect upon soil gas concentrations of the fumigants. This can be seen in contrasting soil gas distribution under the two films, where greater concentrations and wider distribution under the VIF were observed.

TABLE 2. Arithmetic Mean (n = 2) and Range of Emissions (% of Total Applied) from Each Chamber Compartment within Each Experimental Treatment

		<i>cis</i> 1,3-D	trans 1,3-D	СР
HDPE	bed	24 (±4)	22 (±4)	7.4 (±0.5)
	sidewall	3.5 (±0.3)	2.0 (±1.1)	0.19 (±0.07)
	furrow	0.07 (±0.02)	0.06 (±0.03)	0.01 (±0)
	drip total	28	24	8
	shank total ^a	42	37	1.1
VIF	bed	0.58 (±0.29)	0.24 (±0.17)	0.02 (±0.01)
	sidewall	0.40 (±0.22)	0.29 (±0.25)	0.03 (±0.02)
	furrow	12 (±1)	6.9 (±0.9)	1.4 (±0.8)
	drip total	13	7	1.5
	shank total ^a	2.3	2.5	0.0008

^a Comparative data for simulated shank injection (30 cm depth) to same soils (nonbedded) under same films, where whole soil surface was covered with film (1).

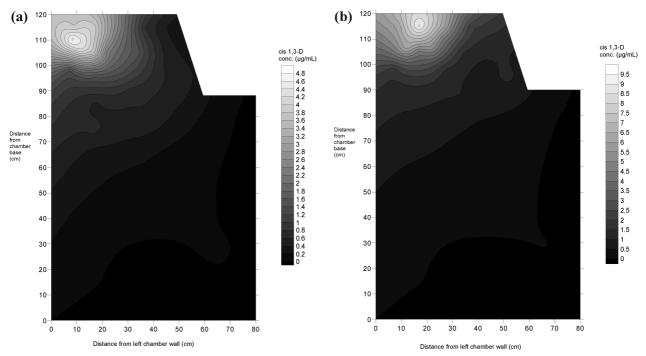


FIGURE 2. Soil gas cis 1,3-D concentrations under (a) HDPE and (b) VIF after 24 h.

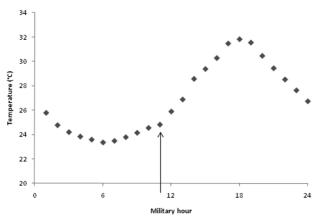


FIGURE 3. Repeating 24 h diurnal pattern in soil temperature at 5 cm depth. Arrow shows timing of fumigant application (11:00 h; Time 0 in Figure 1a and b).

The maintenance of high soil gas fumigant concentrations is critical in ensuring successful pest disinfestation. In addition, the presence of fumigants throughout the bed region of the chambers at 24 h suggests that the application procedure was effective in facilitating fumigant distribution within the crop rooting zone. Overall, comparing the two films, the higher total emissions from HDPE covered soil would be likely to have a greater negative impact in relation to air quality, for example, via contribution to near-surface ozone formation. In addition, this relatively large loss from the soil led to low soil gas concentrations and potentially less efficacious pest control.

For comparison to the emission fluxes, the 24 h diurnal pattern in soil temperature measured at 5 cm depth within the chambers is presented in Figure 3. The influence of soil temperature is evidenced by the higher fluxes generally corresponding to afternoon and early evening times. Due to its influence over vapor pressure, the role of soil temperature in influencing the rate of 1,3-D (*10*, *11*) and CP (*8*) volatilization from bare soil, has been previously reported. In covered soils, the effect of temperature on the permeability of the plastic film must also be considered since increasing perme-

ability of plastic film at higher temperatures has been reported (4, 6), and differing films may exhibit differing temperaturedependent permeability. This is again consistent with the observed increases in emission fluxes during the warmer parts of the temperature cycle. Although both films appeared to exhibit this effect, the VIF seemed to be most strongly affected; exhibiting many fluctuations in emission flux over time. It has been reported that low density polyethylene (LDPE) may be more strongly affected by temperature than VIF (12).

The type of plastic film clearly had a marked impact on the point of fumigant release from the bed furrow system. With the higher permeability HDPE, the emission release of both 1,3-D and CP from the three headspace compartments followed the order bed > sidewall > furrow. This would be the expected pattern based on the positioning of the fumigant application and would also be the expected pattern for a nontarped raised bed system. It has been reported (8, 9) that the vast majority of fumigant emissions occurred from the bed surface with bare soil or relatively permeable plastic covering (e.g., HDPE, LDPE, and semi-impermeable film). In contrast, our current data show that emissions from the VIF treatment were always greatest from the furrow. It seems therefore, that the very low permeability of this film, evidenced by the very low level of emissions directly above the application point (i.e., from the bed compartment), resulted in the diffusive transport of the fumigant both vertically and horizontally. Since both the bed and sidewall were covered with the VIF, the furrow base was the only region from which emissions could readily occur. Consequently, a delay in emissions from the furrow was observed due to the time taken for gas diffusion to this region. Indeed, the broad nature of the flux rate curve from the VIF chamber (Figure 1b) is mostly due to this emissions delay.

In sand mesocosms and field studies (13), similar results using the same VIF (Hytibar) were reported; noting that the majority of *cis/trans* 1,3-D, MITC and propargyl bromide emissions occurred from the furrow following drip application. In practical terms, the fact that more than 90% of the total fumigant emission from the VIF treatment occurred from the furrow (Table 2), indicates that a supplementary emission reduction strategy applied to the furrow may be beneficial. A possible approach may be the furrow application of a chemical amendment (e.g., thiosulfate solution) to enhance fumigant degradation in this region. Potassium thiosulfate used in the furrows of VIF covered beds reduced CP emissions from 17% (VIF only) to 11% (*12*). However, in LDPE covered beds, the thiosulfate did not yield further emission reductions over plastic film alone.

Comparison of the present data with literature data suggest that when 1,3-D and CP are applied under plastic films but in the absence of excess irrigation water and to nonbedded systems (e.g., shank/broadcast applied), total emissions are greater than observed in the present study. For a field study (3), 1,3-D (cis + trans) emissions for shank injection (46 cm) under HDPE of 43% and for VIF 19% were reported. For CP, the values were 17% and 8%, respectively. These values are higher than those observed in Table 2 for the same treatments. In the same study, these workers also determined 1,3-D emissions of 12%, and CP emissions of 2% from a drip application at 20 cm depth under HDPE. This greater depth may explain the lower emissions than were found in the present study. Also in field studies (14), CP emissions of 9.5 and 18% for two soils following shank injection at 20-25 cm under HDPE were found. For simulated shank injected CP in column studies, emissions of 20% under HDPE and 4% under VIF (15), and 30% under HDPE (16) have been reported. For 1,3-D, emissions of 45% under HDPE, and 10% under VIF, for a 30 cm simulated shank injection to soil columns were observed (17). Overall, these comparisons suggest an emissions benefit in the application of fumigants with drip irrigation to raised bed systems.

However, in a recently published paper (1), we reported data for 1,3-D and CP emissions from laboratory soil columns where a simulated shank injection was made at 30 cm depth to nonbedded soil completely covered with plastic film. The soil, plastic films and application rate were the same as those used in the present study and so provide a useful basis for comparing the two simulated application scenarios. Only in the case of 1,3-D (both isomers) under HDPE did the dripapplied, raised-bed application lead to a reduction in fumigant flux rates when compared to the shank injection. Peak emission of the cis isomer was reduced from around $29\,\mu g\,m^{-2}\,s^{-1}$ to around 14.5 $\mu g\,m^{-2}\,s^{-1}$, and that of the trans isomer from around 23 $\mu g\,m^{-2}\,s^{-1}$ to 10.5 $\mu g\,m^{-2}\,s^{-1}.$ However, within the same treatment, CP emissions doubled with the drip-applied, raised-bed application (peak emission increasing from $5 \mu g m^{-2} s^{-1}$ to around $10 \mu g m^{-2} s^{-1}$). Furthermore, under VIF, emissions of both 1,3-D isomers and CP were increased with the drip-applied, raised-bed application. 1,3-D isomer flux values were typically around an order of magnitude greater, and CP around 2 orders of magnitude greater, compared to shank injection. When emissions are expressed as a percentage of the total amount of fumigant added to the system, clear differences between the application methods were again observed. Total emissions from the shank injected soils were, under HDPE: cis 42%; trans 37% and CP 1.1%. And under VIF: cis 2.3%; trans 2.5% and CP 0.0008%. Comparing these values (Table 2), it is evident that total emissions of cis and trans 1,3-D were both lower with the drip/raised-bed application under HDPE, but that in all other cases this application resulted in higher total emissions than the shank injection.

We believe that the reason the drip/raised-bed application did not produce lower emissions of 1,3-D and CP under VIF was due to the furrow region of the chambers not being covered with film. As is evident in Table 2, the majority of emissions from the VIF chambers occurred from this region, that is, the fumigants diffused to this region through the soil because they could not pass through the highly impermeable film over the bed/sidewall surface. In contrast, with the shank injection under VIF, the entire soil surface was covered with the film and resulted in very low emissions. The same is not true for HDPE because of its greater permeability, that is, the vast majority of emission occurred from the bed surface (Table 2). Under HDPE, the 1,3-D and CP clearly behaved very differently in relation to application method and we believe this may have been due to differences in their physical/chemical properties. Although they exhibit similar solubility, the dimensionless Henry's constant of CP is significantly higher than that of both *cis* and *trans* 1,3-D. Indeed, Wang et al. (18) indicated a CP value almost twice that of cis 1,3-D and almost three times that of trans 1,3-D (Table 1). Therefore, under conditions of drip irrigation, trans 1,3-D would be expected to most readily remain in the water phase and CP to more readily convert to the gas phase (with cis 1,3-D intermediate). With the drip application taking place much closer to the soil surface than the shank application, a conversion of CP to the gas phase soon after drip application would likely lead to higher emissions, that is, due to a short path length to the soil surface. For the 1,3-D isomers, their greater affinity for the water phase likely led to solute transport to greater depths with the irrigation water, and an increased path length to the soil surface. In combination with fumigant partitioning into the liquid phase and the clogging of soil pores by the irrigation water, this will have led to reduced emissions compared to the shank injection.

Overall, the results suggest that, compared to HDPE, VIF can offer significant reductions in emissions of 1,3-D and CP from raised bed systems. 1,3-D under HDPE was the only combination that followed the expected behavior of reduced emissions from drip-applied, tarped, raised-beds when compared to shank injection under plastic film. On this basis, we conclude that further direct comparisons (i.e., using the same soils, plastic films, and experimental conditions) between shank and drip application systems are required to fully determine emission reduction benefits of either approach.

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Literature Cited

- Ashworth, D. J.; Ernst, F. F.; Xuan, R.; Yates, S. R. Laboratory assessment of emission reduction strategies for the agricultural fumigants 1,3-dichloropropene and chloropicrin. *Environ. Sci. Technol.* 2009, 43, 5073–5078.
- (2) Ajwa, H. A.; Trout, T.; Meuller, J.; Wilhelm, S.; Nelson, S. D.; Soppe, R.; Shatley, D. Application of alternative fumigants through drip irrigation systems. *Phytopathology* 2002, 92, 1349– 1355.
- (3) Gao, S.; Trout, T. J.; Schneider, S. Evaluation of fumigation and surface seal methods on fumigant emissions in an orchard replant field. *J. Environ. Qual.* **2008**, *37*, 369–377.
- (4) Wang, D.; Yates, S. R.; Gan, J.; Knuteson, J. A. Atmospheric volatilization of methyl bromide, 1,3-dichloropropene and propargyl bromide through two plastic films: Transfer coefficient and temperature effect. *Atmos. Environ.* **1999**, *33*, 401–407.
- (5) Papiernik, S. K.; Yates, S. R.; Gan, J. An approach for estimating the permeability of agricultural films. *Environ. Sci. Technol.* 2001, 35, 1240–1246.
- (6) Papiernik, S. K.; Yates, S. R. Effect of environmental conditions on the permeability of high density polyethylene film to fumigant vapors. *Environ. Sci. Technol.* **2002**, *36*, 1833–1838.

- (7) Noling, J. W.; Becker, J. O. The challenge of research and extension to define and implement alternatives to methyl bromide. *J. Nematol.* **1994**, *26*, 573–586.
- (8) Ashworth, D. J.; Ernst, F. F.; Yates, S. R. Soil chamber method for determination of drip-applied fumigant behavior in bedfurrow agriculture: application to chloropicrin. *Environ. Sci. Technol.* 2008, 42, 4434–4439.
- (9) Van Wesenbeeck, I. J.; Knuteson, J. A.; Barnekow, D. E.; Philips, A. M. Measuring flux of soil fumigants using the aerodynamic and dynamic flux chamber methods. *J. Environ. Qual.* 2007, *36*, 613–620.
- (10) Ashworth, D. J.; Yates, S. R. Surface irrigation reduces the emission of volatile 1,3-dichloropropene from agricultural soils. *Environ. Sci. Technol.* 2007, *41*, 2231–2236.
- (11) Basile, M.; Senesi, N.; Lamberti, F. A study of some factors affecting volatilization losses of 1,3-dichloropropene (1,3-D) from soil. *Agric. Ecosyst. Environ.* **1986**, *17*, 269–279.
- (12) Qin, R.; Gao, S.; McDonald, J. A.; Ajwa, H.; Shen-Tov, S.; Sullivan, D. A. Effect of plastic tarps over raised-beds and potassium thiosulfate in furrows on chlorpicrin emissions from drip fumigated fields. *Chemosphere.* **2008**, 558–563.
- (13) Papiernik, S. K.; Yates, S. R.; Dungan, R. S.; Lesch, S. M.; Zheng, W.; Guo, M. X. Effect of surface tarp on emissions and distribution of drip-applied fumigants. *Environ. Sci. Technol.* **2004**, *38*, 4254–4262.
- (14) Wang, D.; Juzwik, J.; Fraedrich, S. W.; Spokas, K.; Zhang, Y.; Koskinen, W. C. Atmospheric emissions of methyl isothiocyanate

and chloropicrin following soil fumigation and surface containment treatment in bare-root forest nurseries. *Can. J. For. Res.* **2005**, 35, 1202–1212.

- (15) Gan, J.; Yates, S. R.; Ernst, F. F.; Jury, W. A. Degradation and volatilization of the fumigant chloropicrin after soil treatment. *J. Environ. Qual.* 2000, *29*, 1391–1397.
- (16) Zhang, Y.; Wang, D. Emission, distribution and leaching of methyl isothiocyanate and chloropicrin under different surface containments. *Chemosphere* 2007, 68, 445–454.
- (17) Gao, S.; Trout, T. J. Using surface water application to reduce 1,3-dichloropropene emission from soil fumigation. *J. Environ. Qual.* 2006, *35*, 1040–1048.
- (18) Wang, D.; He, J. M.; Knuteson, J. A. DripFume: A visual basic program for simulating distribution and atmospheric volatilization of soil fumigant applied through drip irrigation. *Comput. Electron. Agric.* 2007, *56*, 111–119.
- (19) Thomas, J. E.; Hartwell, A.; McCormack, L. A.; Vu, J. C.; Dickson, D. W.; Ou, L. T. Diffusion and emission of 1,3-dichloropropene in Florida sandy soil in microplots affected by soil moisture, organic matter, and plastic film. *Pest Manage. Sci.* 2003, 60, 390–398.
- (20) California Department of Pesticide Regulations. Use Information and Air Monitoring Recommendations for Field Fumigations with the Pesticide Active Ingredients 1,3-Dichloropropene, Chloropicrin, Metam Sodium, and Methyl Bromide; CDPR: Sacramento, 2001.

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