Annual Report to the Almond Board of California

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Project: Minimizing Emissions from Soil Fumigation

Project Leader: Tom Trout
USDA-ARS, Parlier, CA
SJVASC, 9611 S. Riverbend Ave.,
Parlier, CA 93648
Phone: 559-596-2852
FAX: 559-596-2851
E-mail: ttrout@fresno.ars.usda.gov

Co-Investigator: Suduan Gao, USDA-ARS, Parlier, CA

Cooperating Personnel: Greg Browne, Sally Schneider, Husein Ajwa

BACKGROUND INFORMATION

Methyl bromide (MeBr) is being phased out internationally as a stratospheric ozone depleting compound. Some alternatives [e.g., 1,3-dichloropropine (1,3-D), chloropicrin (CP), and metam sodium (MITC generator)] have been increasingly used in recent years. Fumigants are regulated primarily based on their toxicology and air emissions. Minimizing emissions will be critical to maintaining or achieving practicable restrictions for alternative fumigants.

Emissions from soil fumigation are affected by soil conditions (texture and soil moisture), climatic conditions, and conditions at the soil surface that inhibit fumigant movement (surface seals). Surface plastic mulch reduces emissions for fumigants, but is expensive (about $600 per acre for purchase, placement, removal, and disposal of standard HDPE tarps). Plastic tarps do improve pest treatment of surface soil – especially weed control. High soil moisture and slight compaction at the soil surface also reduces emissions by reducing air-filled pore space. For some fumigants such as Telone, high soil moisture is a more effective barrier to fumigant movement than HDPE (Gan et al 1998). The Telone label requires adequate surface soil moisture before fumigation is allowed.

Reduced emissions also can improve efficacy by holding the fumigant in the soil longer. This can allow use of lower rates. However, high soil moisture in the soil can reduce fumigant distribution and efficacy. Thus, it is critical that water applied for surface sealing be applied uniformly and to the desired depth and moisture content. This will require proper soil preparation and water application by sprinkler systems near the time of fumigation. Although this process will complicate fumigation, regulations will require low emissions, and proper soil and water preparation will be less expensive than plastic tarps.

OBJECTIVES

To develop practical cultural and irrigation practices that minimize fumigant emissions from the soil and allow practical use of MeBr alternative fumigants.

EXPERIMENTS AND RESULTS

This 3-year project is designed to test application methods, including shank injection and drip application, and surface sealing techniques, including surface water seals, soil compaction, and tarps, on air emissions and fumigant distribution in soil profiles of alternative fumigants. Laboratory soil column experiments and field trials were planned to test various treatments.

During the first year of the project, we conducted one field trial in Sierra Gold Nursery and determined fumigant emissions and distribution in soil profile between broadcast shank injection and drip application methods under standard high density polyethylene (HDPE) tarp. We conducted soil column experiments and determined the potential of surface water application (water seal) in reducing emissions. One field trial to test water seal technique on reducing emissions was scheduled in spring, 2005 but we were unable to complete it because of the wet soil profiles from the rain in May. This trial is delayed and will be carried out during July of 2005. The following will report research findings from the Sierra Gold Nursery field trial that was conducted in fall, 2004 and the soil column experiment in spring, 2005.

Sierra Gold Field Trial

The purpose of this trial was to determine emission and distribution or movement of fumigants (Telone C35 and Midas) in soil profile in both gas phase and liquid/solid phase under different fumigation methods (i.e., shank injection vs. drip application) under HDPE tarp.

Soil in the Sierra Gold Nursery trial is Yokohl clay loam (fine, montmorillonitic, thermic, Typic Durixeralfs). The surface (0-15 cm) was the dry tilled layer and had a bulk density of 1.30 g/cm^3. From 15 to 50 cm, soils were moist, dark colored, and fine textured, and had a bulk density of 1.35 g/cm^3. At and below 50-60 cm depth, soils were moister, light reddish colored, and gravely fine textured. A hard duripan was present near these depths. The bulk density was 1.55 g/cm^3.

Methods

This field trial was designed to test fumigation methods and nematode control (efficacy) for several alternative fumigants. There were total 8 treatments with 5 replicates. All plots were 25 ft wide and the length was 50 ft for drip application treatments and 100 ft for shank injection treatments. For the purpose of monitoring emissions and fumigant distribution in soil profiles, we chose four plots with the following treatments:

Treatment 4: Shank/Telone C35 (61%1,3-D, 7% CP; 544 lb/A, shank injection spacing=10", depth=18" (45 cm), disk/ring roller; standard HDPE tarp.

Treatment 5: Shank/Midas (67% MeI, 33%CP); 300 lb/A; shank injection spacing=12", depth=12" (30 cm), no disk roller; standard HDPE tarp.

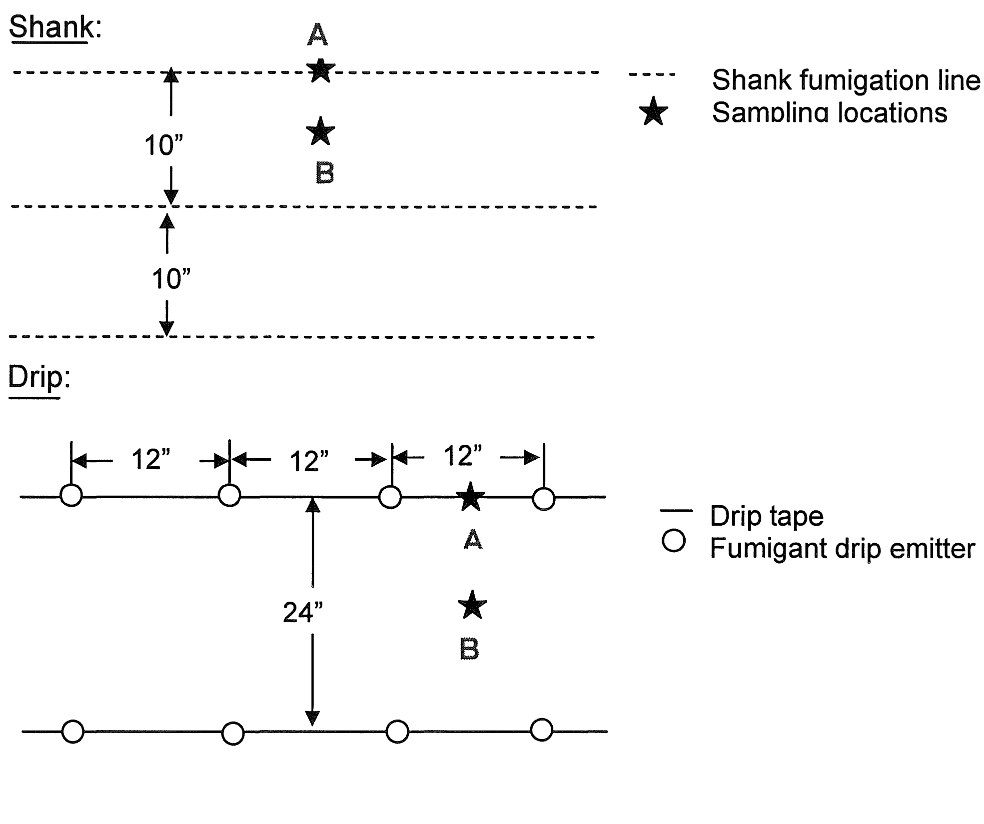
Treatment 7: Drip/InLine (61% 1,3-D, 7% CP); 544 lb/A; drip tape spacing=24", emitter spacing=12", depth=4" (10 cm); standard HDPE tarp.

Treatment 8: Drip/Midas (67% MeI, 33% CP); 300 lb/A; drip tape spacing=24", emitter spacing=12", depth=4" (10 cm); standard HDPE tarp.

For drip application, fumigant formulation was injected in 3.5" water and delivered over an 18-hour period through drip tape buried at 4" (10 cm) depth.

To monitor fumigant distribution in soil, stainless-steel gas sampling probes were installed just after fumigation. The sampling locations are shown in Figure 1, and include adjacent to where fumigant was applied from shank emitters or drip tapes (Location A) and between shank injection emitters or drip tapes (Location B). At different times after fumigation (up to 4 days), 50 mL of soil air was withdrawn with a gas-tight syringe and the air was pulled through an ORBO XAD 4 sampling tube that adsorbs fumigants. The ORBO tubes were stored above dry ice in a cooler, transferred to freezer in the lab, and extracted with hexanes for analysis for fumigants using an Agilent GC-MS system.

For sampling emissions, closed chambers were placed on the plot (three replicates). The chamber was sealed on the HDPE tarp with a silicone sealant. A Teflone faced silicone septum was installed at the top of the chamber. Thirty minutes after placing the chambers, 120 mL of gas samples were withdrawn with a gas tight syringe through the septum. Similar procedures were followed as sampling soil gas samples for storage, extraction and fumigant analysis.



Results

Emissions:

Emission fluxes from Telone C35 and Midas from shank injection and drip application are shown in Figures 2 and 3. For Telone C35, drip application resulted in higher emission fluxes than shank injection; but the opposite is true for Midas application, i.e., drip application resulted in lower emission than shank injection. There might be two reasons for the lower shank emission of Telone C35. Some of the shank outlets were clogged during application and only 84% of scheduled amount was injected in the monitoring plot. This was also verified by the monitored chemical data in soil gas phase. The drip application took about 18 hours and emission measurement was carried out after fumigation was complete. Thus the lower emission rates from the shank injection of Telone C35 need to be checked in future field trials. For Midas, however, shank application applied 137% of scheduled amount. The scheduled amounts of fumigants were applied in drip application for both Telone C35 and Midas. From Midas application, drip application resulted in clearly lower emission rates than that from shank injections. Due to the mixed application rates of fumigants in shank injection, emission results would need to be verified with future field trials.

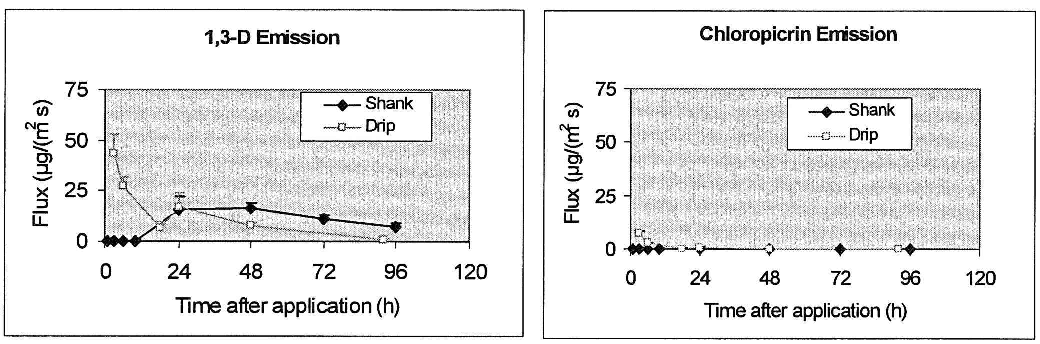


Figure 2. 1,3-dichloropropene and chloropicrin emissions from Telone C35 (shank application) and InLine (drip application) fumigation with HDPE tarp.

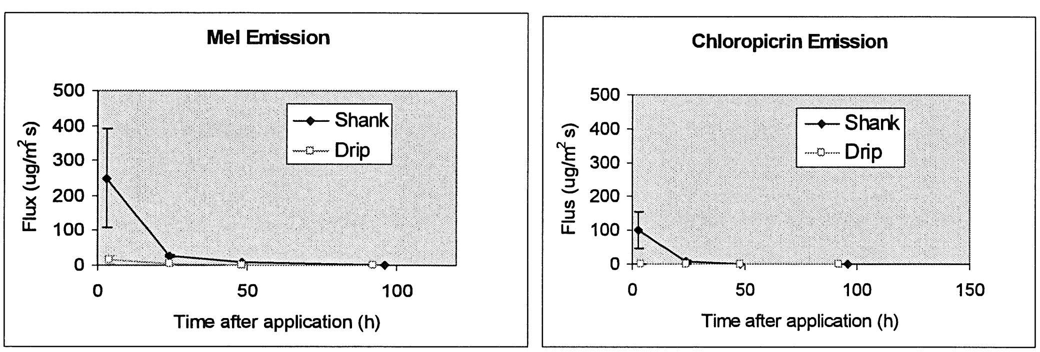


Figure 3. Methyl iodide (MeI) and chloropicrin emissions from Midas fumigation through shank and drip applications with HDPE tarp.

Distribution of fumigants in soil profile:

Figure 4 shows the distribution of fumigants in soil profile after application of Midas (data for Telone C35 is not shown). Shank injection resulted in a more even distribution of fumigant in soil profiles as there were no differences in MeI concentrations between Location A (adjacent to injection line) and Location B (between injection lines). However, for drip application, there were significant differences in fumigant concentrations between Location A (drip tape) and Location B (between drip tapes), i.e., fumigant concentration in the B location is much lower than that near the drip tapes. This indicates that fumigant movement was not reaching to the distance of 12” from the drip tape in this soil. This may indicate that the designs used in this trial for this fumigant did not yield a good distribution of fumigants in the soil and this could result in poor pest control.

Fumigant downward movement in soil profile was restricted to less than 60 cm. Drip application appeared to move fumigant to deeper layers than shank injection because the highest concentration was observed at 30 cm although the drip injection depth was 10 cm. Shank injection resulted in the highest concentration at 20 cm or above with injection depth of 30 cm.

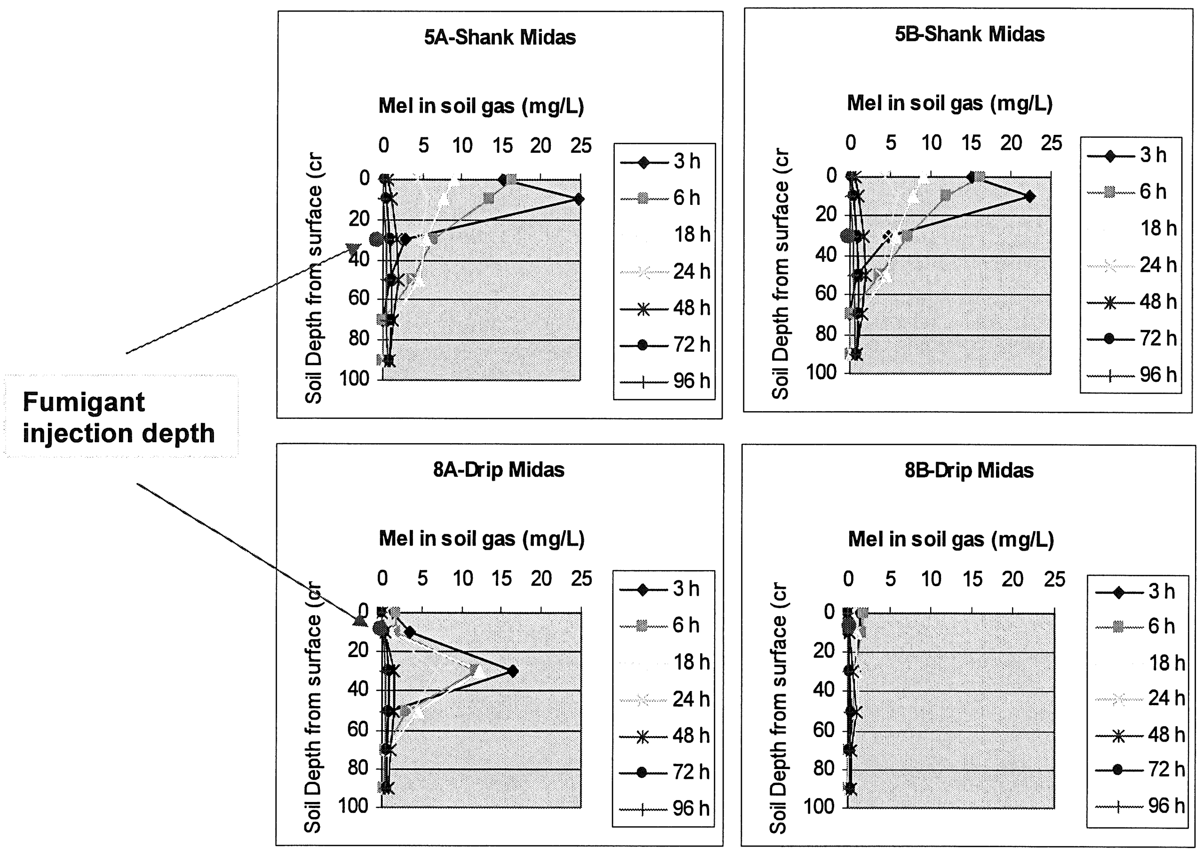


Figure 4. Methyl iodide distribution in soil gas phase after application of Midas

Soil water content:

Soil water content changes after fumigation through shank and drip applications are shown in Figure 5. As expected, drip application resulted in higher water content in the surface soils (0-50 cm) than that from shank application plots. As shown above, the water content has impact on fumigant movement in the soil profile as well as emissions. There is no clear understanding on the optimum soil moisture condition that reduces emissions while maintaining good pest control efficacy. This condition will vary among soils and fumigants.

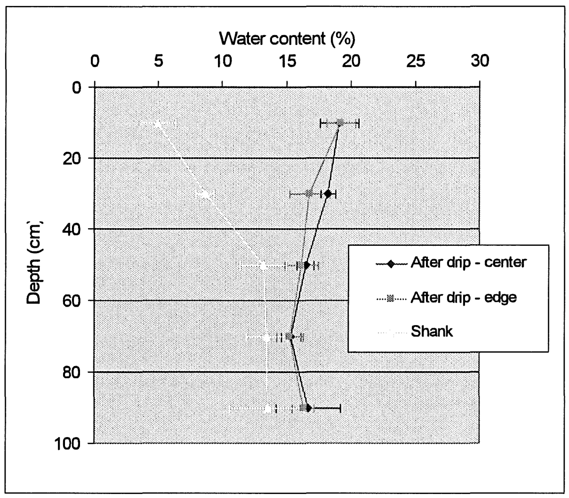


Figure 5. Water content increases following drip fumigation in a clay loam soil (center=near drip tape; edge=between drip tapes)

Summary from Sierra Gold Field Trial

Due to the varied application rates of fumigants in shank injections, emission results are mixed in comparing shank injection to drip application. Drip application resulted in higher emission rates than shank injection for Telone C35 but lower emission fluxes for Midas. Drip application resulted in a larger spatial variation (uneven distribution) in fumigant concentrations than shank application. This observation is more evident for MeI than 1,3-D. Generally speaking, fumigant concentrations in soil gas phase were higher in shank applications compared to drip application; but the opposite is true in liquid/solid phase (data not shown). Fumigant movement was limited to a depth of about 60 cm, possibly due to the application depth and the presence of a duripan layer in this clay loam soil. Soil water content may help deliver fumigants but may inhibit fumigant distribution as well. An optimum soil moisture condition that reduces emissions while maintaining good pest control efficacy may depend on soil type and fumigant property.

Soil Column Experiment

The purpose of the soil column study was to determine the potential of using surface water application (or water seal) after fumigation in reducing emissions and the impact on fumigant distribution in soil.

Methods

A Hanford sandy loam soil was used to pack soil in stainless steel columns [63.5 cm high x 15.5 cm (i.d.)]. The soil column was packed with a bulk density of 1.4 g/cm^3. Surface water was applied to the top surface layer using a spray bottle. When used, the tarp was sealed at the top edge of the stainless steel columns. For sampling soil gas, sampling ports were installed at depths of 0, 10, 20, 30, 40, 50, and 60 cm below the soil surface. A Teflon-faced silicon septum was installed in each sampling port. Soil gas was withdrawn through the sampling port with a gas-tight syringe. For sampling emissions, a flow-through gas sampling chamber, which had the same diameter as the soil column, was placed on the top of the soil column and was sealed to the bottom column with a sealant-coated aluminum tape. After the whole soil column was constructed and treatment was applied, a continuous flow rate between 100-120 mL/min was maintained by vacuum throughout the study period of 2 weeks.

Fumigants of 100 µL cis 1,3-D (122 mg) and 40 µL (66 mg) chloropicrin were injected into the column center at the 30 cm depth. This gives a mass ratio of 1,3-D to CP of 2:1, a similar composition of fumigants in Telone C35. The following treatments were used: 1. Dry soil and no tarp (Control). 2. Initial water application by adding 148 g (or 16 mm) water to the soil column surface. This amount of water can wet the surface soil to 5 cm depth. 3. Same as Treatment #2 followed by a second water application (49 g or 2.6 mm) at 12 h after fumigant injection. 4. Same as Treatment #3 followed by a third water application of 49 g water at 24 h. 5. Dry soil with HDPE tarp. 6. Initial water application (same as Treatment #2) plus HDPE tarp. 7. Dry soil with VIF tarp.

The time fumigants were injected into the soil column was considered time zero. For measuring emissions, ORBO™ 613, XAD 4 80/40mg tubes were connected into the outlet of the top air chamber to adsorb fumigants off the column surface. Five mL of hexane were used to extract materials in each tube after breaking into 10 ml clear headspace vial following the method by Guo et al., (2003). Fumigants in the extracts were analyzed by an Agilent GC-MS system (Agilent Technologies 6890 Network GC system, and 5973 Inert Mass Selective Detector). A DB-VRX capillary column (30-m length x 0.25 mm-i.d. x 1.4 µm film thickness) was used for separation of the fumigants. The ORBO tubes were frozen if extraction could not be done immediately.

For fumigant concentration in soil gas phase, 0.5 ml volume of soil gas was withdrawn with a gas-tight syringe at times of 1, 3, 6, 12, 24, 36, and 48 h followed by 3, 4, 7, 9, 11, and 14 d after fumigant injections. The gas sample was injected to a 21-ml headspace clear vial and the vials were immediately crimp-sealed with an aluminum caps and Teflon-faced butyl-rubber septum. If analysis could not be done immediately, the vials were stored in an ultra freezer at a temperature of -44 °C. All samples were analyzed within 72 h, a stable period of time for fumigants in laboratory conditions. The analysis was carried out using a GC-μECD (Agilent Technology 6890N Network GC system with a micro electron capture detector) and an automated headspace sampler (Agilent Technologies G1888 Network Headspace Sampler) system. Similarly, a DB-VRX capillary column was used with the same dimension as the fumigant analysis above.

Results

Emission Reduction:

Emission flux: The emission fluxes for 1,3-D and CP from the column treatments are shown in Figures 6 and 7, respectively. In the control, flux increased, peaked (~1.1 mg h^{-1} $column^{-1}$) at about 15 h after fumigant injection, and gradually decreased thereafter. The initial 16 mm water applied right before fumigant injection delayed fumigant volatilization from the column and also reduced the peak flux to 0.7 mg h^{-1} $column^{-1}$ at 15 h. The treatment that included initial water (16 mm) application followed by 2.6 mm water application at 12 h after fumigant injection showed abrupt reduction of 1,3-D emission at 12 h. The treatment that included two intermittent water applications (2.6 mm) at 12 h and 24 h after fumigant injection repeated this abrupt reduction at 24 h. The abrupt drop of emission flux presents the immediate impact of surface water application on emissions. Use of HDPE tarp shows a similar degree of emission reduction as the initial surface water application. Initial water application plus HDPE tarp had additional reduction of emissions. The maximum reduction of 1,3-D emissions was from VIF tarp, which shows extremely low emissions. The water application at 12 h and 24 h can reduce flux to 0.1 mg $column^{-1}$ h^{-1}, close to the level with VIF tarp. Although VIF had extremely low emissions, materials are expensive and installation problems are not yet solved.

Treatment effects on chloropicrin emission flux basically show the same pattern as 1,3-D, except much lower values than expected were measured. Further, the reduction of relative emission of CP appears much greater than 1,3-D (Table 1). With the low amount of CP applied, degradation of CP may dominate in the soil columns that resulted in low emissions.

Total emissions: Figure 7 shows the cumulative emission and Table 1 shows the percentage of emissions compared to the control for each treatment. Initial water application just before fumigant injection reduced emissions by delaying the peak time and also reduced the peak emission rates compared to the control. Total emission reductions from intermittent water applications were more effective within the first couple of days compared to the whole 2-week period of time because water application was accomplished within 24 h after fumigation. Intermittent water application reduced emissions equally or more compared to the use of HDPE tarp. This indicates that using surface water application has a potential to reduce emission for less cost than using tarps. VIF yielded the lowest total emission, i.e., reduced emission the most. Table 1 shows that initial water plus HDPE tarp is more effective in reducing CP emission than for the 1,3-D. Intermittent water application, i.e., (initial 16 mm + 2.6 mm at 12 h + 2.6 mm at 24 h) is as effective as or even more effective than HDPE alone to reduce emissions for CP but less effective for 1,3-D. This confirms previous reports that HDPE reduces CP emissions more effectively than 1,3-D emissions.

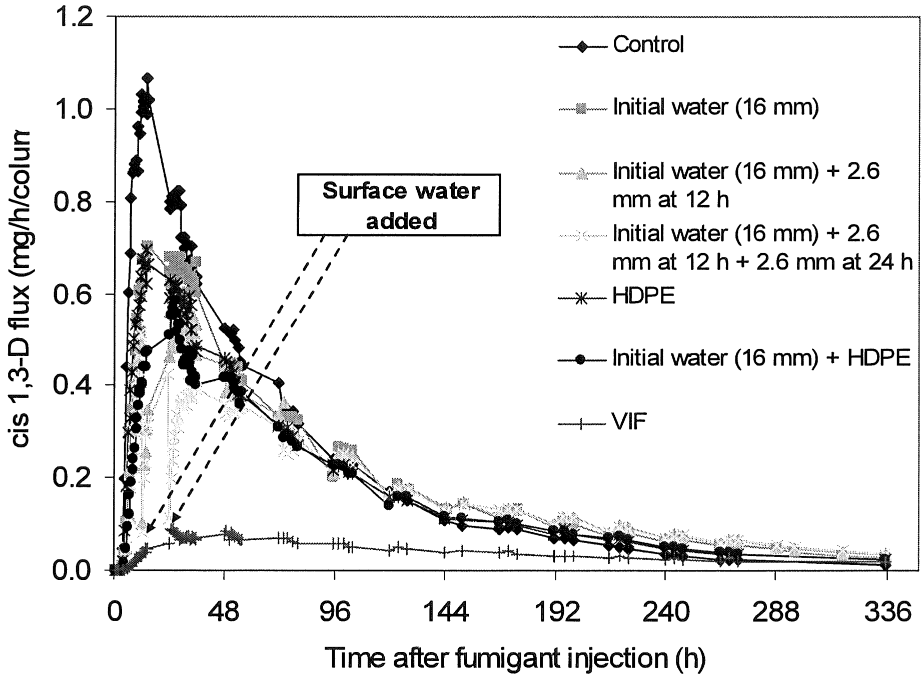


Figure 5. 1,3-D emission fluxes from soil column treatments

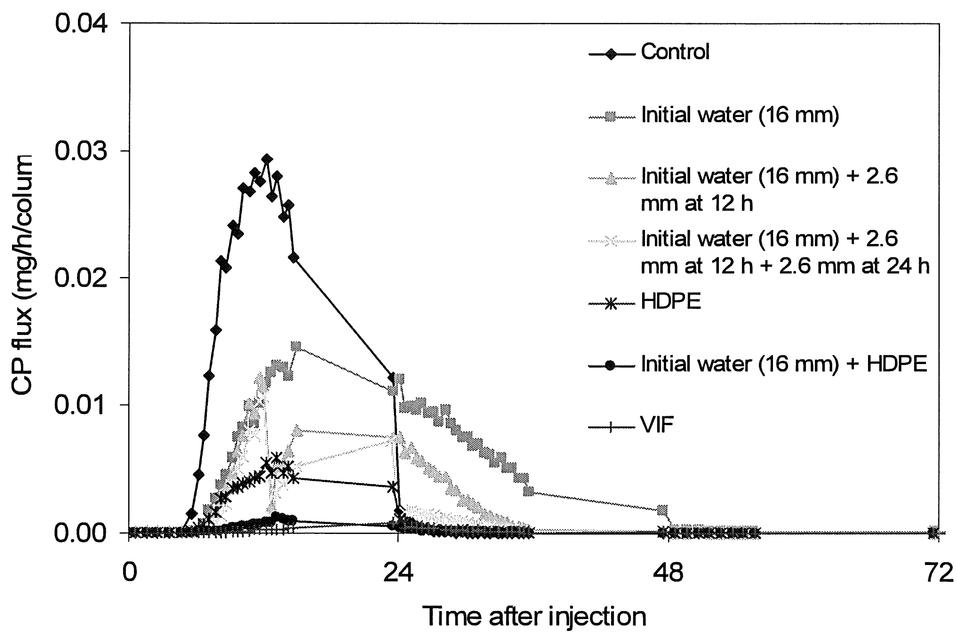


Figure 6. Chloropicrin emission fluxes from soil column treatments

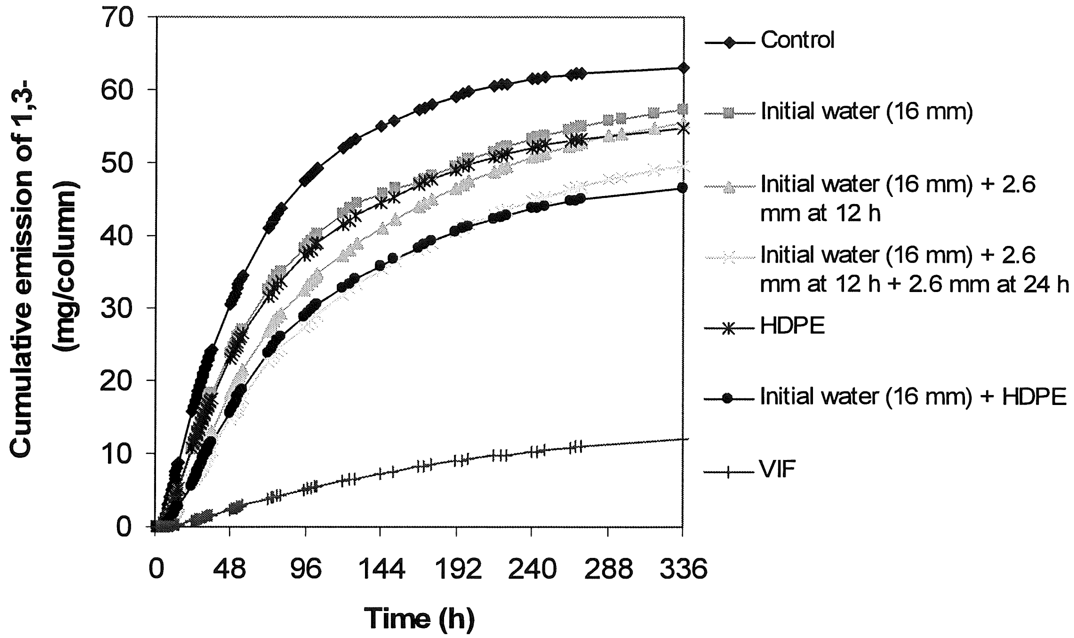


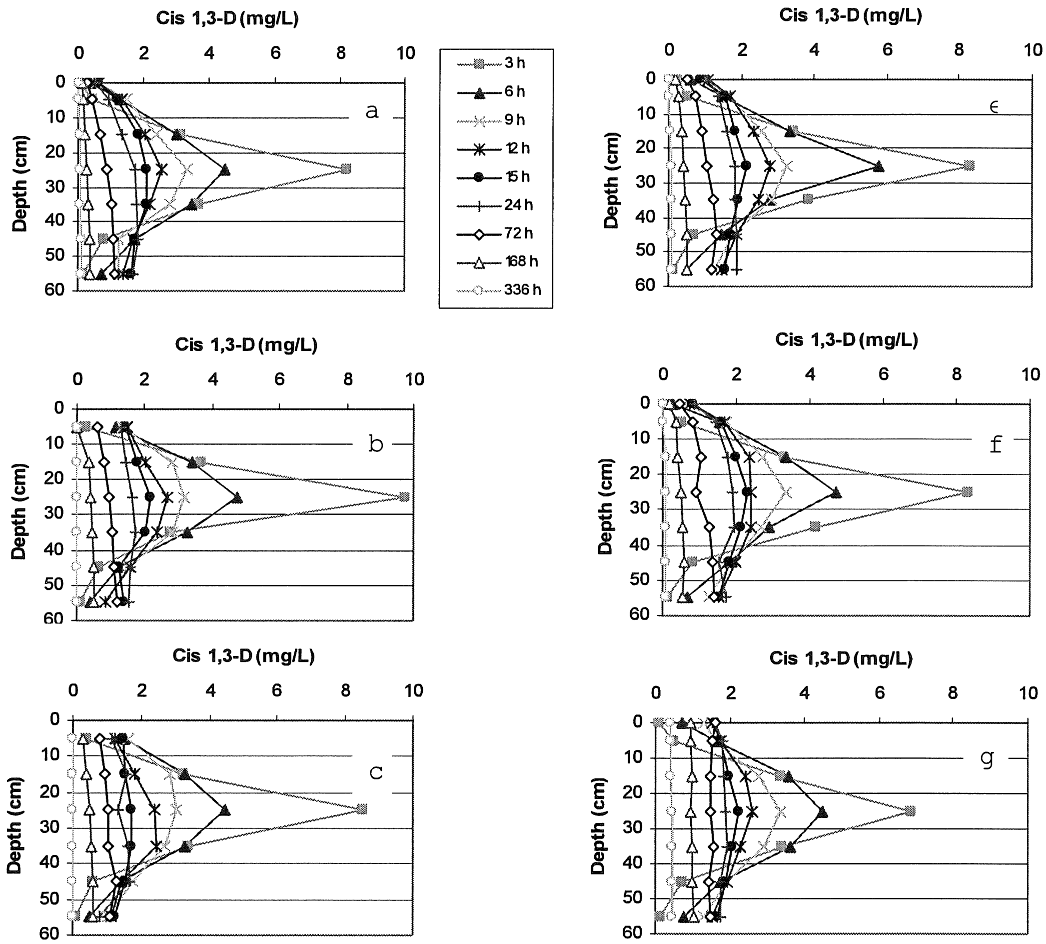
Figure 7. Cumulative 1,3-D emission loss from soil column treatments

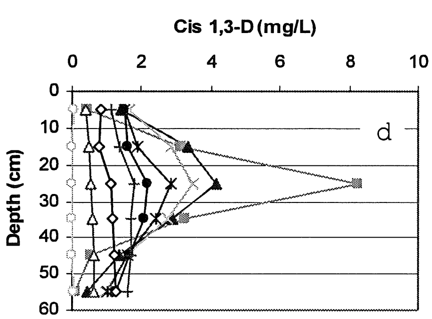
Table 1. Percent of emission from column treatment compared to control

Time (h)	Control	Initial water (16 mm)	Initial water (16 mm) + 2.6 mm at 12 h	Initial water (16 mm) + 2.6 mm at 12 h + 2.6 mm at 24 h	HDPE	Initial water (16 mm) + HDPE	VIF
			1,3-D				
24	100.0	67.3	43.2	40.6	69.3	35.7	4.9
72	100.0	79.3	65.3	54.6	76.7	57.8	9.2
336	100.0	90.7	87.9	78.5	86.8	73.5	19.2
			CP				
24	100.0	66.2	33.7	31.7	20.7	3.4	2.6
72	100.0	80.6	59.7	34.9	21.8	4.2	3.7
336	100.0	80.7	60.7	35.7	21.8	4.6	3.8

Fumigant distribution in soil gas phase

The distribution of 1,3-D in the soil gas phase after fumigant application is shown in Fig. 8. Chloropicrin showed similar pattern except disappearance from the column was much faster than 1,3-D. There are no visual differences in terms of the highest concentrations observed at time 3 h near injection port. The fumigant concentration reached the highest level at the bottom sampling port at 12-15 h. After this time, fumigant tended to disperse through the column to an even profile due to the closed column bottom. The concentration of 1,3-D in soil gas phase decreased to below 0.1 mg/L by the end of the experiment in most of the columns except the VIF treatment where about 0.4 mg/L 1,3-D was still detected. This indicates that VIF tarp that reduces emission the most does hold the fumigant the longest inside soil profile.





Treatment:
a. Control
b. Initial water (16 mm)
c. Initial water (16 mm) + 2.6 mm at 12 h
d. Initial water (16 mm) + 2.6 mm at 12 h + 2.6 mm at 24 h
e. HDPE
f. Initial water (16 mm) + HDPE
g. VIF

Figure 8. Distribution of 1,3-D in soil gas phase from soil column treatments.

Summary from column experiment

Surface water application can reduce fumigation emission as effectively as using standard HDPE tarp. Fumigant concentrations in soil gas phase were not reduced with the amount of water applied in this study indicating that fumigation efficacy should not be affected. Intermittent water application is the key to maximize reduction of emissions. As using water is less expensive than using plastic tarp, surface water application using sprinkler system has great potential to reduce fumigation emissions. In this study, the effect of surface water application on reducing chloropicrin emission showed more effective than 1,3-D under the conditions studied indicating that there are differences between fumigants. The results indicate that there are field practices that can reduce fumigant emissions.

Our next step is to conduct field trials with small plots to test and develop practices that can reduce emissions while maintaining good pest control efficacy. These practices include fumigation methods (shank vs. drip application), use of plastic tarps (HDPE vs. VIF), and surface water application (or water seal) for alternative fumigants to methyl bromide.

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