Chapter 9

Reducing 1,3-Dichloropropene Air Emissions in Hawaii Pineapple with Modified Application Methods

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Restrictions on 1,3-dichloropropene (1,3-D) use in California due to air quality concerns prompted the testing of improved application methods in Hawaii. Strategies investigated for their impact on 1,3-D air emissions include (1) a comparison of one and two soil chisels per bed, (2) polyethylene mulch films which cover one or two beds, and (3) an emulsified liquid formulation of 1,3-D (SL) applied by drip irrigation compared with chisel injected 1,3-D. Air concentrations were measured at a 15-cm height above the soil to compare 1,3-D emissions near the source. Measurements of spatial and temporal distributions of 1,3-D in soil gas and in soil profiles complemented air monitoring. A single chisel per bed (45 cm depth) reduced 1,3-D air emissions compared with double chisels (30 cm depth). Wide mulch film did not reduce air emissions in a single field trial. Although drip irrigation application of 1,3-D resulted in reduced air emissions, 1,3-D soil distribution was sub-optimal compared with chisel injection.

Preplant soil fumigation is widely practiced in Hawaii's pineapple industry to control plant parasitic nematodes in soil (*1,2*). At present, 1,3-dichloropropene (1,3-D) and methyl bromide are the two soil fumigants in widespread use. Recent legislation phasing out the

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use of methyl bromide by the year 2001 (*3*), has prompted pineapple companies to evaluate alternative fumigants, as well as non-volatile nematicides for preplant nematode control. In 1990, the use of 1,3-D was restricted in California due to potential negative impacts on the air quality during spring fumigations (*4*). Regulatory action in California prompted the pineapple industry to evaluate air emissions resulting from the current use patterns of 1,3-D in Hawaii (Hawaii Department of Agriculture, unpublished report). The industry began testing reduced application rates of 1,3-D and new application methods to lower air emissions to acceptable levels.

Pineapple growers have typically applied 1,3-D at a rate of 224 to 336 L ha^{-1}. Pineapple was grown in a perennial cropping cycle which yields three fruit harvests from a single planting. In addition, fields were fallowed for 6-12 months after the third harvest. Therefore, each field was fumigated once every 4-5 years. 1,3-D was typically applied by chisel injection to a depth of 30-40 cm, with two chisels spaced 46 cm apart, to correspond to two plant rows per bed. Polyethylene mulch film and drip irrigation tubing were also laid down during the fumigation process.

The objective of our research program was to evaluate the impact of three new application methods on 1,3-D air emissions above treated fields. In each experiment, a new application method was compared with a conventional method by sampling 1,3-D in air at a fixed height (15 cm) above the field within the treated areas. Collecting 1,3-D air samples at a single height allowed us to directly compare emissions between treatments but did not allow us to quantify the flux of 1,3-D from the treated fields. The application methods which were evaluated in four large field experiments were: 1) single chisel injection compared with double chisel injection; 2) wide polyethylene mulch film (2 m wide) compared with narrow polyethylene mulch (0.8 m); 3) drip irrigation application of 1.3-D compared with chisel injection. The single and double chisel injection treatments were evaluated in two field experiments, in 1990 and 1993.

Materials and Methods

Field Experiments.

Field experiments were conducted near Kunia, Oahu, Hawaii in commercial pineapple fields on Del Monte plantation. The field sites are summarized in Table I. Telone II (94 % A.I. 1,3-D, DowElanco) was applied in all four experiments at an application rate of 224 L ha^{-1} using commercial fumigation equipment. Two pineapple beds were fumigated simultaneously with chisels mounted on a tractor which formed the bed, laid polyethylene mulch film and drip irrigation tubing, and applied granular fertilizer during the fumigation operation. In experiments I, II, and III, the soil series was Wahiawa silty clay, an aggregated, well drained Oxisol with a bulk density of 1.0 g cm^{-3}, and an organic carbon content of 1.5 to 2 %. In experiment IV, the soil series was Kunia silty clay, an Inceptisol with similar soil properties, but without stable aggregates. Soil aggregates result in a coarse textured soil with drainage properties similar to sandy soils.

In experiment I, two different chisel injection methods were compared for their effect on air emissions of 1,3-D. In the single chisel treatment, fumigant was injected in the center of the bed at a depth of 45 cm. The double chisel method used two chisels per bed, spaced 46 cm apart, with an injection depth of 35-40 cm. In addition to the chisel treatments, polyethylene mulch film (0.8 m wide, 1 mil thick) was used in treatments 1 and 2, but not treatment 3 (Table I). Treatment blocks varied in size from 0.4 to 3.9 ha and were separated by untreated buffer zones to minimize cross contamination during air monitoring. Field blocks were fumigated with 1,3-D on December 7, 8, and 10, 1990 for treatments 1, 2, and 3, respectively. Three air sampling pumps were centrally located in each treatment at a sampling height of 15 cm above the soil surface. Air samples were collected in 12-hour sampling intervals for 5 days, followed by 24-hour intervals for the remainder of the 10-day sampling period.

Table I. Summary of field experiments used in 1,3-D air monitoring study

Expt.	Treatments	Date (Field)	1,3-D Rates (L ha^{-1} A.I.)	Soil Order	1,3-D Measurements
I	1. Double chisel + mulch	Dec. 1990	224	Oxisol	Air
	2. Single chisel + mulch	(DM-1)			Soil gas
	3. Single chisel, no mulch				
II	1. Single chisel	August 1993	224	Oxisol	Air, Soil gas
	2. Double chisel	(DM-13)			Soil
III	1. Narrow mulch	Sept. 1993	224	Oxisol	Air, Soil gas
	2. Wide mulch	(DM-13)			Soil
IV	1. Drip irrigation	August 1994	224	Inceptisol	Air, Soil gas
	2. Single chisel	(DM-5)			Soil

In experiment II, single and double chisel injection methods were also compared for their effect on 1,3-D air emissions. A new single chisel injector design, a split-depth injector, was used. Two treatment blocks (block size 2.7 ha) separated by an untreated buffer zone (266 m wide) were fumigated with 1,3-D using either single chisel injection or the conventional double chisel method. With the split-depth single chisel injector, 70 % of the fumigant was injected at 45 cm depth and the remaining 30 % injected at 30 cm. Double chisel injection delivered the fumigant to 40 cm depth (chisel spacing of 46 cm). Polyethylene mulch film (0.8 m wide, 1 mil) was used in both treatments. Fumigation of both treatments was accomplished on the same day, August 17, 1993. Two air monitoring stations were established in the center of each treatment block. The air sampling height was 15 cm and the sampling interval was 12-hours during the entire 7-day sampling period.

Experiment III was conducted in September 1993, in the same field as experiment II, to compare two types of polyethylene mulch for their retention of 1,3-D. Two adjacent field blocks (separated by a road, 5 m wide) were fumigated with 1,3-D using single chisel split-depth injection. Treatment 1 was covered with standard narrow polyethylene mulch (0.8 m) and treatment 2 was fumigated using wide mulch (2 m) to cover two planting beds; both mulch films were 1 mil in thickness. Field blocks were fumigated on September 14 and 15, for wide mulch, and narrow mulch treatments, respectively. Two air sampling stations per treatment and 12-hour sampling intervals were used.

In experiment IV, drip irrigation application of 1,3-D SL, an emulsifiable formulation, (XRM-5053, DowElanco, 66 % A.I. 1,3-D) was compared with single chisel injection of 1,3-D (Telone II, 94 % A.I. 1.3-D) using a new chisel design, a winged shank injector developed by DowElanco. Two field blocks, 0.5 and 1.4 ha in size, were fumigated by drip irrigation and single chisel injection, respectively. Polyethylene mulch film (0.8 m wide, 1 mil) was used in both treatments. The two treatment blocks were separated by a buffer zone (365 m) and five air monitors were installed in each treated block, as well as in the center of the untreated zone. 1,3-D SL was applied with 1.9 cm of water, continuously during a 6-hour irrigation cycle. 1,3-D was injected at 45 cm depth in the center of the bed, using the winged-shank injector. The two wings on the injector were offset from the chisel shaft by 7.5 cm on each side; this design minimizes the upward loss of 1,3-D through the chisel trace. Both 1,3-D treatments were applied on August 23, 1994 and 1,3-D air emissions were monitored for 14 days. A 12-hour sampling interval was used for the first 7 days followed by a 24-hour interval thereafter.

Analytical Methods

Air Sampling Methods. Air samples for 1,3-D were collected using SKC air monitoring pumps (Model 224) and coconut charcoal adsorbent tubes (SKC, 10 mm diameter, 800/200 mg) at a pumping rate of 1.25 liters per minute. Pumps were supplied with charged batteries and calibrated with a flow meter at the start of each sampling period. Sample tubes were stored in a freezer soon after collection. Field spikes and blank tubes were included with each day's samples. Air samples from experiments I and IV were analyzed by Dow Chemical Co. using solvent desorption with carbon disulfide and GC-FID or GC-ECD (Dow Chemical Co., unpublished report). Air samples from experiments II and III were analyzed by solvent desorption with acetone and analyzed by GC-ECD (*5*). Charcoal samples were sonicated for 30 minutes in 10 ml of acetone and analyzed by direct injection on a HP5890A gas chromatograph with HP7673A autosampler. Extracts were analyzed using isothermal conditions (70 C) and a DB-1701 column (15 m x 0.53 mm, 1 μm film, J.& W. Scientific). Retention times for cis and trans isomers of 1,3-D were 2.17 and 2.65 minutes, respectively. In laboratory spikes, sample tubes were fortified with 5 μl of Telone II standard (DowElanco, 96 % 1,3-D; cis : trans ratio, 53 : 47) to yield concentrations of 50.7 and 45.1 μg per tube, for cis and trans 1,3-D, respectively. Recovery of 1,3-D averaged 90.6 % (± 4.6) for cis 1,3-D and 93.9 % (± 4.6) for trans 1,3-D. Recovery of 1,3-D from field spikes averaged 81.2 % (± 3.1) and 80.2 % (± 5.1), for cis and trans isomers, respectively. Samples were frozen and analyzed within two weeks of collection. A storage stability study showed no loss of extraction efficiency over a 2-week period.

Soil Gas Method. Soil gas samples were collected and analyzed for 1,3-D during the first seven days after fumigation. Gas samples were collected in two locations, the planting row (23 cm from the bed center), and the interbed (53 cm from bed center). Stainless steel probes (1/8 inch OD) were used to collect gas samples at depths of 5, 15, 30, and 45 cm (*6-7*). Soil probes were sealed with Swagelok unions and rubber septa. Gas samples were collected with 0.5 ml gas sampling syringes (Dynatech A-2) after purging the probe volume by removing 3-ml of air from each probe. Gas samples were stored at room temperature and analyzed within 30 hours of collection by GC-ECD as described for air samples. Soil gas samples (50 μl) were injected manually and cis and trans 1,3-D were quantified with gas standards made from a Telone II standard.

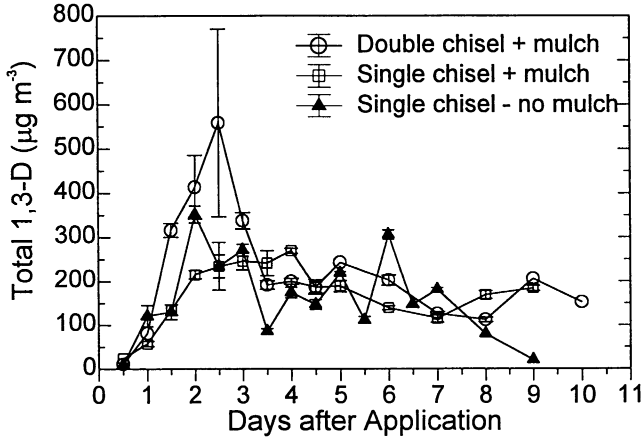

Figure 1. Concentrations of total 1,3-D in air (cis + trans, µg m^{-3}) for experiment I are plotted over a 10-day period after fumigation. Values are means of triplicate samples with standard error bars. (Reproduced with permission from ref. 7. Copyright 1995 Butterworth-Heinemann journals, Elsevier Science Ltd, The Boulevard, Langford Lane, Kedlington 0X5, UK.)

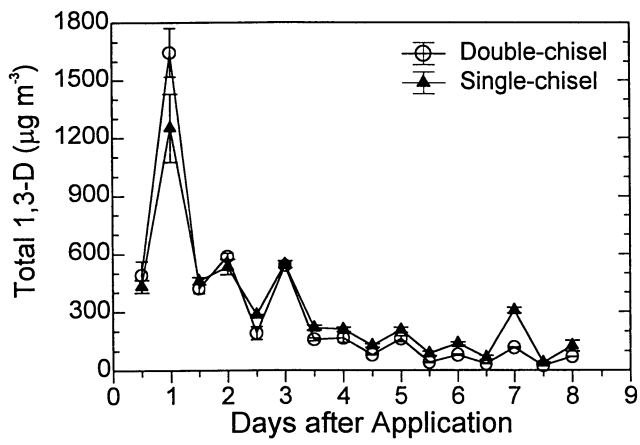

Figure 2. Concentrations of total 1,3-D in air (cis + trans, µg m^{-3}) for experiment II are plotted over an 8-day period. Values are means of duplicate samples with standard error bars. (Reproduced with permission from ref. 7. Copyright 1995 Butterworth-Heinemann journals, Elsevier Science Ltd, The Boulevard, Langford Lane, Kedlington 0X5, UK.)

Soil Sampling Method. Soil samples were collected 7-8 days after fumigation with bucket augers to a maximum soil depth of 90 cm, in 15-cm increments (*6-7*). Soil profiles were sampled from bed center, planting row, and interbed to describe the spatial distribution of 1,3-D in the bed. Soil samples were stored at 4 C for up to four days after collection. Subsamples (50 g) were extracted by co-distillation, using a mixture of 175 ml water and 10 ml hexane (*8*). Sample extracts were analyzed by GC-ECD as described for air samples. In laboratory spikes, soil samples fortified at a concentration of 0.04 $\mu g\ g^{-1}$, yielded average recoveries of 90.3 % (± 7.2) and 82.1 % (± 9.6), for cis and trans 1,3-D, respectively.

Results

In experiment I, conducted in December 1990, 1,3-D air emissions from double chisel fumigation were compared with emissions from two single chisel treatments, with and without mulch film. The target injection depths were 45 cm for the single chisel, and 35-40 cm for the double chisel. The air monitoring results, reported in Figure 1, show much higher 1,3-D air emissions from double chisel fumigation compared to the single chisel. There was little difference in the air emission pattern between the two single chisel treatments. The polyethylene mulch had little or no effect in retaining the fumigant.

In experiment II, conducted in August 1993, a new single chisel design, the split-depth injector, was compared with the double chisel injection method. 1,3-D air emissions for experiment II are plotted in Figure 2. Peak values measured during this experiment were two to three times higher than those measured in experiment I (Figure 1). Both chisel treatments showed similar 1,3-D air concentrations with the exception of the peak values measured 24 hours after fumigation.

The design of experiment III, conducted in September 1993, incorporated split-depth single chisel injection and two types of mulch film, (narrow and wide) to assess the effect of mulch type on 1,3-D air emissions. The 1,3-D air emission pattern measured in this experiment, shown in Figure 3, was quite different from the two previous field trials. There was a large diurnal fluctuation in 1,3-D air concentration, probably as a result of unusual weather conditions. The measured 1,3-D air concentrations showed no treatment differences with the two types of mulch. Peak 1,3-D values, measured 48 hours after fumigation were slightly higher in the wide mulch treatment. Soil gas results from the planting row, plotted in Figure 4, offer an explanation for the lack of treatment differences in the air data. 1,3-D concentrations in soil gas were approximately three times higher in the narrow mulch block than in the wide mulch block. In Figure 4a, 1,3-D soil gas concentrations peaked three days after injection near the targeted split-injection depths, 30 and 40 cm. In the wide mulch block (Figure 4b) peak soil gas levels were measured earlier, two days after injection, at 5- and 15-cm depth. Very low 1,3-D concentrations were detected at 30 and 40 cm (Figure 4b). These data indicate that 1,3-D did not penetrate to the target injection depths in the wide mulch block. It was later confirmed that soil tillage was poor in the wide mulch block, preventing deep penetration of the chisels.

Air emission data from experiment IV, which compared drip irrigation of 1,3-D SL, with chisel-injected 1,3-D, using a winged shank, are plotted in Figure 5. Air monitoring during the first 48 hours after application showed higher 1,3-D emissions from the drip irrigation treatment. The initial air samples, plotted at Day 0, represent a 3-hour interval immediately after application (1530-1830 hours). All other data points represent 12- or 24-hour intervals. The initial differences in 1,3-D air emissions between treatments are

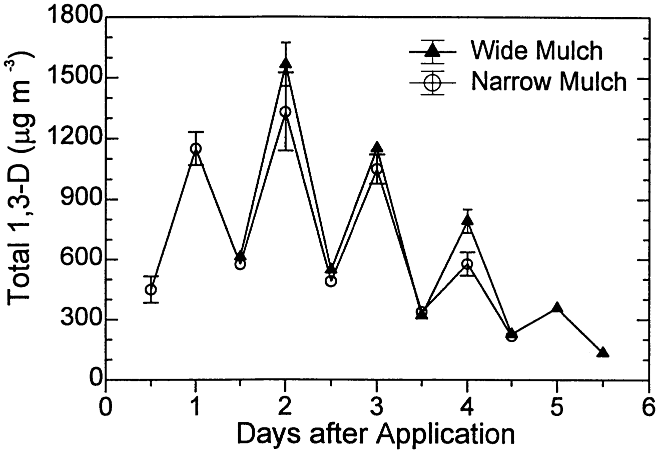

Figure 3. Concentrations of total 1,3-D in air samples (cis + trans, $\mu g\ m^{-3}$) from experiment III are plotted over a 6-day period after fumigation. Values are means of duplicate samples with standard error bars.

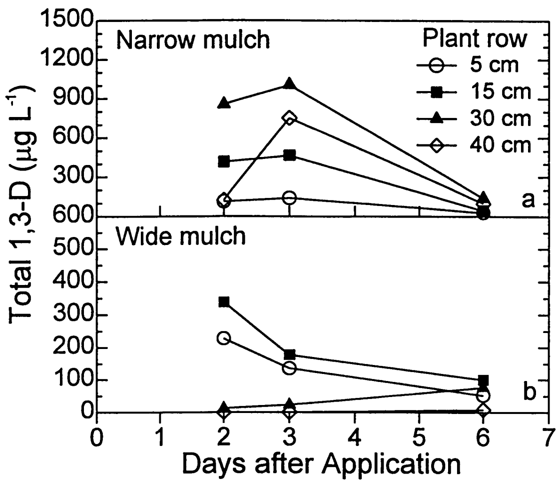

Figure 4. Soil gas concentrations of total 1,3-D (cis + trans, $\mu g\ L^{-1}$) from experiment III collected in the planting row from 4 soil depths. Values are means of 4 replicate samples. a) Treatment 1, single chisel injection with narrow (0.8 m) polyethylene mulch. b) Treatment 2, single chisel injection with wide (2 m) mulch.

attributed to application method. With chisel injection, the fumigant was delivered in a narrow band at 45 cm depth. With drip application, 1,3-D SL was applied continuously with 1.9 cm of water over a 6-hour irrigation period. Irrigation resulted in a wider initial distribution of 1,3-D both vertically and laterally in the planting bed. The soil water content also differed significantly between treatments. The low soil water content (15-25 %) in the chisel treatment represents a soil moisture tension of approximately 100 kPa, compared with 28-33 %, or 10-30 kPa in the irrigated treatment. Soil gas 1,3-D concentrations from the interbed location are plotted in Figure 6. Gas concentrations were relatively low (< 100 $\mu g\ L^{-1}$), and represent loss of 1,3-D from the mulch-covered planting bed. Figure 6b shows a diffuse 1,3-D gas distribution in the drip irrigation treatment with peak values at 45 cm, three days after application. With chisel injection, maximum 1,3-D levels were measured at 30 cm depth, two days after fumigation (Figure 6a). Soil gas 1,3-D values at 5 cm depth were significantly higher with drip irrigation than with chisel injection. These 5-cm soil gas data correlate well with the air emission results (Figure 5) and indicate that greater lateral movement of 1,3-D with drip irrigation resulted in greater loss of 1,3-D from the bed and therefore higher initial air emissions.

Discussion

Of the application methods tested in this study for reducing 1,3-D air emissions, deep single chisel injection was the most promising. The air emission data from the four field experiments indicates that the chisel designs used in experiments I and IV, performed better than the split-depth chisel design. 1,3-D air concentrations ranged from 200 to 600 $\mu g\ m^{-3}$ in those two experiments compared with peak values of 1200 to 1500 $\mu g\ m^{-3}$ measured in experiments II and III, where the split-depth chisel injector was used. With single chisel injection, the distribution of 1,3-D in soil differed markedly from the double chisel method. When two chisels per bed were used, the result was uniform 1,3-D distribution in the bed, whereas the single chisel produced a sharp concentration gradient from the center to the edge of the bed (7). Field studies have shown that single chisel injection is equivalent to double chisel injection in terms of nematode control and crop yield (*2,7*).

Polyethylene mulch films are not usually recommended for use with 1,3-D (*9*), but have been used in Hawaii's pineapple industry since the initiation of 1,3-D fumigation in the 1940's (*10*). Plastic mulch films are used to provide weed control and conserve soil moisture as well as to retain fumigants. Since pineapple is a perennial crop and is drip irrigated, the use of mulch is a valuable component of the cropping system. In experiment I, 1,3-D air emissions were compared for deep single chisel injection, with and without mulch film. The absence of mulch had very little effect on the magnitude of 1,3-D loss to the atmosphere (Figure 1).

Wide polyethylene mulch film (2 m) has been used routinely with methyl bromide fumigation in pineapple and was tested in experiment III for its potential to reduce 1,3-D loss to the atmosphere. Due to the problems with poor soil tillage in that experiment, it was inconclusive whether wide mulch would improve 1,3-D retention. In small research plots, 1,3-D concentrations in soil gas increased along the gradient from no mulch to narrow mulch to wide mulch, indicating the value of plastic mulch in retaining 1,3-D in the soil for a longer period (Schneider, R. C., unpublished data).

Drip irrigation of 1,3-D SL compared favorably with chisel injected 1,3-D in terms of air emissions. The early peak in 1,3-D emission was due to the continuous irrigation

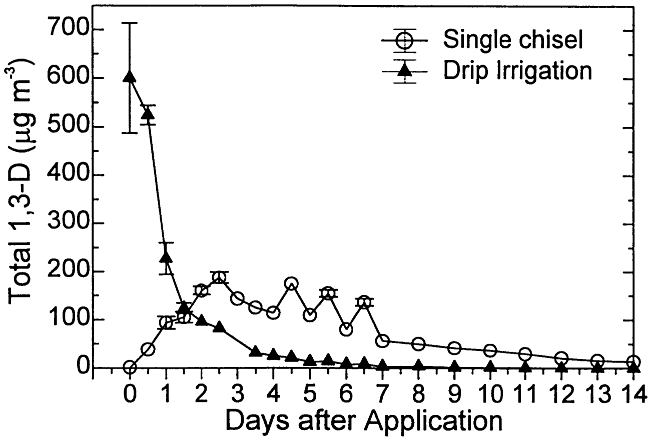

Figure 5. Concentrations of total 1,3-D in air (cis + trans, $\mu g\ m^{-3}$) for experiment IV are plotted over a 14-day period after 1,3-D application. Values are means of 5 samples per treatment with standard error bars.

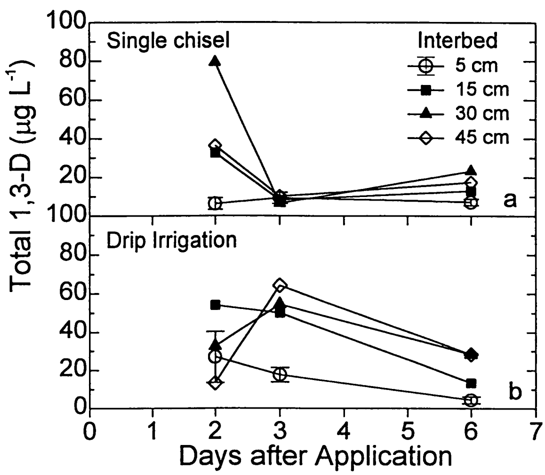

Figure 6. Soil gas concentrations of total 1,3-D (cis + trans, $\mu g\ L^{-1}$) from experiment IV collected in the interbed location from 4 soil depths. Values are means of 6 replicate samples, with standard error bars plotted for the 5 cm depth. a) Drip irrigation application of 1,3-D SL with 1.9 cm water. b) Single chisel injection of 1,3-D fumigant to 45 cm depth with winged shank.

method used, and the large volume of water applied. A modified drip irrigation method, which has been used previously (*6*), is to apply the fumigant formulation in a small volume of water and then post-irrigate with the desired amount of water. This method would reduce the 1,3-D concentration near the soil surface and minimize lateral transport of the fumigant in the bed. The 1.9 cm of water used in experiment IV resulted in a diffuse 1,3-D concentration in the bed, with penetration below the 45-cm pineapple rooting depth. Based on drip irrigation experiments with 1,3-D SL, and non-volatile nematicides in pineapple, (*6,11*) a 1.3 cm irrigation volume should provide a more optimal 1,3-D distribution in soil.

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