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ARTICLE

Effects of Manure and Water Applications on 1,3-Dichloropropene and Chloropicrin Emissions in a Field Trial

SUDUAN GAO,*,† RUIJUN QIN,† BRADLEY D. HANSON,† NISHANTH THARAYIL,† THOMAS J. TROUT,‡ DONG WANG,† AND JAMES GERIK†

†Water Management Research Unit, San Joaquin Valley Agricultural Sciences Center, United States Department of Agriculture−Agricultural Research Service (USDA−ARS), Parlier, California 93648, and ‡Water Management Research Unit, United States Department of Agriculture−Agricultural Research Service (USDA−ARS), Fort Collins, Colorado 80526

Minimizing fumigant emissions is required for meeting air-quality standards. Application of organic materials to surface soil has been effective in reducing fumigant emissions during laboratory tests, but the potential to reduce emissions in the field has not been adequately evaluated. The objective of this study was to determine the effect of incorporated composted manure with or without water applications on fumigant emissions and the potential impact on pest control efficacy under field conditions. Treatments included a bare-soil control, composted dairy manure at 12.4 and 24.7 Mg ha^{-1}, postfumigation intermittent water seals (11 mm water irrigated immediately following fumigation and 4 mm at 12, 24, and 48 h), and incorporation of manure at 12.4 Mg ha^{-1} combined with the water seals or a high-density polyethylene (HDPE) tarp. Telone C35 was shank-applied at 553 kg ha^{-1}, and emissions of 1,3-dichloropropene (1,3-D) and chloropicrin (CP) were monitored for 10 days. The results indicate that there was no significant difference in emission peak flux and cumulative emission loss between the control and the 12.4 Mg ha^{-1} manure treatment. The higher manure rate (24.7 Mg ha^{-1}) resulted in lower emission flux and cumulative emission loss than 12.4 Mg ha^{-1}, although the differences were only significant for CP. In contrast, the water treatments with or without manure incorporation significantly reduced peak emission rates (80% reduction) and cumulative emission loss (~50% reduction). The manure + HDPE treatment resulted in the lowest CP emissions but slightly higher 1,3-D emissions than the water treatments. Reductions in peak emission from water treatments can be important in reducing the potential acute exposure risks to workers and bystanders. This research demonstrated that incorporation of composted manure alone did not reduce fumigant emissions and effective emission reduction with manure amendment may require higher application rates and/or more effective materials than those used in this study.

KEYWORDS: Soil fumigation; emission reduction; high-density polyethylene tarp; volatile organic compounds

INTRODUCTION

Soil fumigation is commonly used in several high-value cropping systems in California, including strawberry, annual, and perennial crop nursery production, perennial crop replant situations, and some vegetables. Emissions of chemicals used as soil fumigants must be minimized to reduce the potential exposure risks to workers and bystanders during fumigation and air pollution from emitted toxic or volatile organic compounds (VOCs) (*1*−*3*). Stringent regulations have been developed to improve air quality in ozone non-attainment areas in California (*2*, *3*), and these regulations have created formidable challenges to crop production. For example, perennial nurseries in California rely heavily on fumigation because they are required by regulation to deliver clean (nematode-free) planting materials (*4*). Minimizing fumigant emissions will allow continued availability of fumigants to growers while meeting environmental safety standards.

As of January 2005, methyl bromide (MeBr) was phased out in developed countries because it was identified as a substance contributing to ozone depletion in the stratosphere. However, limited use of MeBr continues for those crops with approved critical use exemptions (CUEs) and treatments meeting quarantine/preshipment (QPS) criteria. Following the regulations, use of alternatives, such as 1,3-dichloropropene (1,3-D), chloropicrin (CP), and methyl isothiocyanate generators (e.g., metam sodium),

*To whom correspondence should be addressed. Telephone: +559-596-2870. Fax: +559-596-2800. E-mail: suduan.gao@ars.usda.gov.

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has increased dramatically (*5, 6*). In addition to toxic properties, most of these alternatives are also VOCs and their use has been highly regulated to minimize the impact on air quality.

Application of composted manure to soil has shown effectiveness in degrading fumigants and reducing emissions of fumigants including MeBr and its alternatives in laboratory studies (*7−9*). Dungan et al. (*10*) evaluated composted steer and chicken manure that were incorporated into surface 5 cm of soil at 3.3 and 6.5 kg m^{-2} (or 33 and 65 Mg ha^{-1}, respectively) to reduce emissions from a drip-applied emulsified formulation of 1,3-D in raised beds. Their results showed that cumulative emission loss of 1,3-D over 170 h was 48 and 28% lower from the steer and chicken manure amended beds, respectively, than from the unamended beds. The cumulative emission loss was not significantly different between the two application rates for both materials. In another field trial, however, a treatment with composted manure spread over the soil surface (i.e., not incorporated into soil) at 12 Mg ha^{-1} under a high-density polyethylene (HDPE) tarp did not reduce emission loss compared to the control (*11*). Overall, there is some evidence that organic amendments have the potential to be practical and low-cost means of reducing fumigant emissions. However, there is insufficient information to establish effective amendment methods to reduce emissions. More information is needed on specific soil/environmental conditions (e.g., soil moisture) required for maximizing this effect from broadcast shank injection of fumigants under field conditions. The objective of this research was to determine the effect of soil amendment with composted manure with or without water applications on fumigant emission reduction and the potential impact on pest control efficacy under field conditions. The efficacy study results related to this research on selected nematodes, pathogens, and weeds were reported by Hanson et al. (*12*).

MATERIALS AND METHODS

Field Trial and Treatments. A field trial was conducted at the USDA−ARS San Joaquin Valley Agricultural Sciences Center (latitude, 36° 35′ 36.74″ N; longitude, 119° 30′ 48.71″ W) at Parlier, CA. The soil was Hanford sandy loam (coarse-loamy, mixed, superactive, non-acid, thermic Typic Xerorthents), and properties of the soil were reported in earlier studies (*13*). During the field trial in November 2007, the daily maximum, minimum, and average air temperatures were in the range of 17−24, 2−10, and 9−15 °C, respectively.

A field site (160 m long and 10 m wide) was cultivated to a 75 cm depth and irrigated 2 weeks before fumigation to achieve adequate soil moisture conditions for the application. Soil water content determined 2 days before fumigation averaged 12.0% (v/v) (45% of field capacity) in the top 50 cm of soil. To determine the effect of organic amendment on fumigant (1,3-D and CP) emissions, the following surface treatments applied to the field were monitored following fumigation: (1) control, (2) manure at 12.4 Mg ha^{-1}, (3) manure at 24.7 Mg ha^{-1}, (4) manure at 12.4 Mg ha^{-1} + HDPE tarp, (5) water seals (11 mm water sprinkler applied immediately following fumigation and three subsequent applications of 4 mm water at 12, 24, and 48 h, respectively), and (6) combination of treatments 2 and 5 (manure at 12.4 Mg ha^{-1} + water seals).

The HDPE tarp (0.025 mm thickness) was obtained from Tyco Plastics, Princeton, NJ. Composted manure was obtained from Earthwise Organics (Bakersfield, CA) and used for all manure treatments, except treatment 4. The composted material was made from 100% dairy manure feedstock and was prepared using a windrow composting process. The windrows had water added and were mechanically turned on a frequent basis. Active compost was maintained under aerobic conditions at a minimum temperature of 55 °C and a maximum of 65 °C for a pathogen reduction period extending 15 days or longer to successfully undergo "processes to further reduce pathogens (PFRPs)", as described in Title 14, California Code of Regulations Section 17868.3. During the period, there was a minimum of five turnings of the windrow. Duration in the windrows is typically 90−120 days, after which it was stockpiled for several months. The composted materials had an average water content of 65%, organic matter of 37%, ash of 64%, total N of 1.6%, total P (P_2O_5) of 1.8%, and total K (K_2O) of 2.8% (all on a dry weight basis) (Joe Voth, personal communication, Paramount Farming Company, Bakersfield, CA, 2008).

All manure application rate treatments refer to fresh weight [measured average water content of 55% (w/w)]. The manure material was spread evenly over the soil surface within a 3 × 9 m plot prior to fumigation and was incorporated into surface (about 15 cm) soils with a disk and roller operation following fumigant application. The incorporation was restricted to surface soils to ensure that the organic material would react with fumigants only near soil surface and would not reduce fumigant concentration (and pest control efficacy) in the deeper soil profile. Treatment 4 was included to compare to a similar treatment tested in a previous trial (*11*) when the manure was not incorporated to the soil and the material was composted steer manure obtained from a local garden supply store. The manure application rates of 12.4 and 24.7 Mg ha^{-1} (~5 and 10 tons per acre) represent commonly used soil amendment rates for maintaining/improving soil physiochemical properties in conventional farming.

On November 12, 2007, 553 kg ha^{-1} Telone C35 (61% 1,3-D, 35% CP, and 4% inert ingredient) was shank-applied (TriCal, Inc., Hollister, CA) using a rig with 9 shanks spaced 50 cm apart and a 45 cm injection depth. After fumigant injection, the surface soil was compacted with a disk and a ring roller followed by tarp placement and irrigation treatments. Water seal treatments were applied with quarter-circle sprinklers that were installed at each corner of the 9 × 9 m plots. All operations including manure incorporation and installation of tarps were completed within 30 min after fumigant application. The initial water seal application started about 3 h following fumigation and took about 1.5 h to complete. The 11 mm of water was sufficient to moisten the top 10 cm of soil to field capacity. Subsequent water (4 mm) applications at 12, 24, and 48 h took about 25 min each. The small water applications were designed to remain near the soil surface to have less of an impact on fumigant distribution (or pest control) in the soil profile. All treatments were replicated 3 times in a randomized complete block design. The blocks and treatments were distributed along a 160 m long strip of the field.

Emission Measurement. Emission monitoring was carried out for 10 days following fumigant application. Emission sampling for both 1,3-D and CP was performed using dynamic flux chambers that were constructed on the basis of similar designs reported by Gao et al. (*14*) and Wang et al. (*15*). This chamber system consists of two components: a flow-through chamber and an automated sampling and data module. The dynamic flux chambers allow for continuous sampling during the course of the monitoring period. More detailed information about the chamber system is provided in Gao et al. (*16*). The flow-through chambers cover a soil surface area of 51 × 25 cm for emission measurement. The chambers were installed near the center of each treatment plot (total 18 plots), perpendicular to shank lines after fumigant injection. A constant air flow (5 L min^{-1}) was maintained through the chamber using a vacuum source. The inflow air was collected 10 m away from the plots and 3 m above the ground through a PVC pipe with a diameter of 10 cm. The inflow air was sampled to obtain background levels of each fumigant, which turned out to be negligible. A small portion (100 mL min^{-1}) of the outflow air was sampled by a split sampling line with XAD sampling tubes (ORBO 613, XAD 4 80/40 mg, Supelco, Bellefonte, PA) for trapping both 1,3-D and CP. For the first 3 days, two XAD sampling tubes were used in series to avoid breakthrough during the high emission flux period; single XAD tubes were used to collect subsequent samples. Sampling tubes were changed every 3 h for the first 4 days and every 6 h thereafter for the remaining days in this trial. At the end of each sampling period, the XAD tubes were stored in a cooler with dry ice in the field and transferred to a freezer at −80 °C in the lab.

Soil Gas Sampling. Fumigants in the soil gas phase were sampled using two sets of stainless-steel tubing with 0.1 mm inner diameter inserted into the soil with the lower ends at depths of 10, 30, 45, 60, and 90 cm below the surface. These probes were installed at two locations for each treatment (locations a, at shank or fumigant injection line, and b, between shank lines). Soil gas samples were collected 6, 12, 24, 48, 72, 96, 120, 168, and 240 h after fumigation. A total of 50 mL of soil gas from each probe was withdrawn with a gastight syringe through an XAD sampling tube.

The XAD sampling tubes were stored and analyzed in the same way as the emission sampling tubes.

Soil Sampling and Other Measurements. Soil samples from the surface down to a 70 cm depth were collected 2 weeks after fumigation to determine residual fumigants. Samples were collected with a bucket auger, mixed immediately, and placed in a screw-top glass jar that was stored on dry ice in the field and in a freezer (−80 °C) in the laboratory until processing. Soil water content was determined. Soil temperature at 10 cm below the soil surface was measured using a Traceable thermometer for 1 day during the trial.

Sample Extraction and Analysis. The XAD sampling tubes were extracted with hexane and analyzed for fumigants following procedures described in Gao and Trout (*13*). The 1,3-D isomers (*cis*- and *trans*-1,3-D) and CP in the extracts were analyzed using a gas chromatograph (Agilent Technology 6890N Network GC system) with a microelectron capture detector (μECD, Agilent Technology, Palo Alto, CA). The separation column was a DB-VRX capillary column (30 m length × 0.25 mm inner diameter × 1.4 μm film thickness, J&W Scientific, Palo Alto, CA). The GC carrier gas (He) flow rate, inlet temperature, and detector temperature were set at 2.0 mL min^{-1}, 140 °C, and 300 °C, respectively. The oven temperature program was set initially at 65 °C, increasing at 2.5 °C min^{-1} to 84 °C. The retention time for *cis*-1,3-D, *trans*-1,3-D, and CP were 5.2, 5.9, and 6.6 min, respectively. The detection limit of the method was 0.01, 0.01, and 0.001 mg L^{-1} for *cis*-1,3-D, *trans*-1,3-D, and CP, respectively, when an injection volume of 1 μL solution and a split ratio of 100 were used. These values translate to detection limits of 0.01, 0.01, and 0.001 μg cm^{-3} for gaseous fumigant in soil and 0.01, 0.01, and 0.001 mg kg^{-1} residual fumigant in soils with the extraction and analysis protocols used in this study. The reported 1,3-D results are the sum of *cis*- and *trans*-1,3-D isomers.

Soil sample extractions were performed following procedures in Guo et al. (*17*). This method can extract >95% of fumigants in soil. Various amounts of Na_2SO_4 (at a 7:1 ratio of Na_2SO_4/soil water) were placed into a 25 mL crimp-top extraction vial prior to soil sample addition. Without defrosting, 8 g equivalent dry weight of soil was weighed into the vial, followed by adding 8 mL of ethyl acetate. The vial was crimp-sealed with aluminum caps and Teflon-faced butyl-rubber septum, mixed, and incubated at 80 °C in a water bath overnight (~18 h). The supernatant, separated from the solids by centrifugation, was analyzed for the fumigants using the GC−μECD as described above, except using ethyl acetate as the standard and sample solvent.

Statistical Analysis. SAS 9.2 (*18*) was used to determine treatment effects on fumigant peak emission flux shortly after fumigation, cumulative emission loss, soil residual fumigant concentrations, surface soil water contents, and temperature. A general linear model (Proc GLM) was used to conduct the analysis of variance (ANOVA), and treatment means were separated using Fisher's protected least significant difference (LSD) procedure with $\alpha = 0.05$.

RESULTS AND DISCUSSION

Emission Flux. Measured emission flux for 1,3-D and CP is shown in **Figure 1**. The control and manure treatment at 12.4 Mg ha^{-1} gave the highest and similar emission rates for both 1,3-D and CP for the first 4 days following fumigation. The manure treatment at 24.7 Mg ha^{-1} was relatively lower than the control and 12.4 Mg ha^{-1} manure treatment. The peak emissions for these three treatments occurred about 30 h after fumigant injection and were significantly higher than the other three treatments (**Table 1**). Emission rates followed diurnal temperature patterns and were highest from 1200 to 1500 h daily and lowest around 0300 h. The water application treatments with or without manure application resulted in the lowest emission rates for 1,3-D within the first 4 days. The manure + HDPE tarp treatment had low peak flux values that were similar to the water treatments (**Table 1**).

For the control and manure amendment treatments, emission flux decreased dramatically with time after the peak flux, had similar values as the water treatments at day 5 or 6, and continued

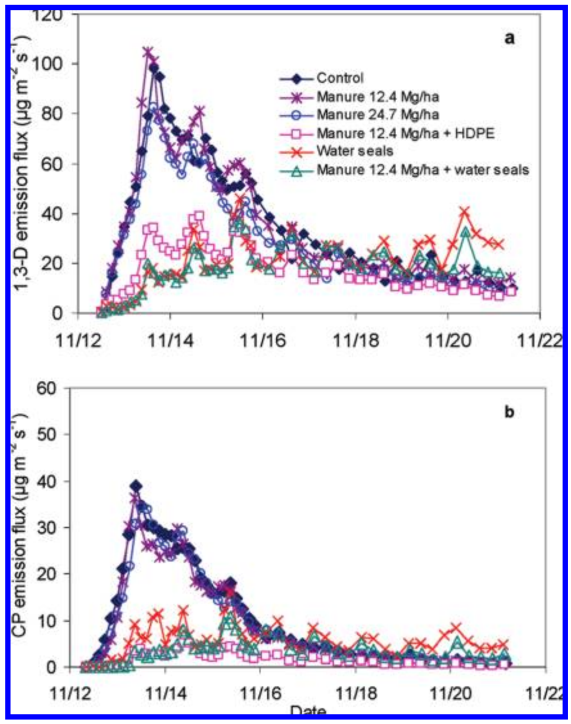

Figure 1. Effects of manure and water applications on emission flux of (a) 1,3-D and (b) CP. Plotted data are averages of three replicates. Error bars are not given to improve the legibility of the figure (significant differences between treatments are indicated in **Table 1**). Manure, composted manure; HDPE, high-density polyethylene.

to decrease thereafter. For the two water treatments (with and without manure amendment), emission flux remained similar during the 10 day monitoring period. At the end of the monitoring period, the water seals only had the highest flux, which was significantly higher than all other treatments for 1,3-D and CP, except the manure + water seal treatment. The manure + HDPE tarp treatment had the lowest emission flux for CP among the treatments throughout the experiment (**Figure 1**), indicating the effectiveness of HDPE to control CP emissions compared to 1,3-D. Similar results had been observed in previous studies (*13*, *19*).

Cumulative Emission Loss. Cumulative emission losses of 1,3-D and CP (**Figure 2**) were calculated on the basis of the measured emission flux data. The fumigant application rate was 33.7 g m^{-2} for 1,3-D and 19.4 g m^{-2} for CP. Calculation for cumulative emission loss over the 10 day monitoring for the control was about 80% of the total applied. This value appears unreasonably high considering the relatively moist soil and low temperature during the field trial in comparison to values reported in the literature (*11*, *13*, *19*). Yates et al. (*20*) discussed that the dynamic chambers had a tendency to overestimate emissions. This could be especially true if a negative pressure (vacuum) was created inside the chamber because of the constant flow. Using the conditions set up in the field, measurements in both laboratory and field resulted in a negative pressure reading of <10 Pa inside the chamber, which is less than 0.01% difference of an atmosphere (*16*). Although there was no data on fumigants, Reichman and Roston (*21*) indicated that pressure deficits larger than 1.2 Pa in a dynamic flux chamber caused a 20% overestimation in measured steady-state flux using chlorofluorocarbon (Freon) as the source. The second possible source of error was from chamber and sample flow recording with McMillan flow meters used. Water condensation may have contributed to erroneous air flow readings. For example, we occasionally observed that in the early mornings (when condensation

Table 1. Emission Peak and Cumulative Emission Loss of 1,3-D and CP Monitored over 10 Days Following Fumigation

	maximum emission flux[a] (μg m^{-2} s^{-1})		cumulative emissions[b] (g m^{-2})	
treatment[c]	1,3-D	CP	1,3-D	CP
control	98.0 a	38.8 a	26.0 a	7.4 a
manure 12.4 Mg ha^{-1}	104.9 a	36.3 a	26.3 a	6.2 ab
manure 24.7 Mg ha^{-1}	72.8 ab	30.7 a	21.5 ab	6.9 a
manure 12.4 Mg ha^{-1} + HDPE	33.3 bc	3.3 b	13.0 b	1.2 d
water seals	16.7 c	3.4 b	16.5 b	4.3 bc
manure 12.4 Mg ha^{-1} + water seal	20.0 c	3.4 b	14.4 b	2.7 cd

[a] Within a column, means ($n = 3$) with the same letter in parentheses are not significantly different according to Fisher's protected LSD test ($\alpha = 0.05$). [b] The fumigant applied was about 33.7 g m^{-2} 1,3-D and 19.4 g m^{-2} CP. The cumulative emission loss of 1,3-D for the control was substantially higher than expected, about 80% of the applied on the basis of the measured emission flux using dynamic flux chambers. Contributed errors might include potential vacuum inside the chamber and malfunction of flow meters because of water condensation in the field. Estimated correction factors for the measured emission loss were 20−40% less. Reported values here were used for a comparison of the relative difference between surface treatments. [c] Manure, composted manure; HDPE, high-density polyethylene.

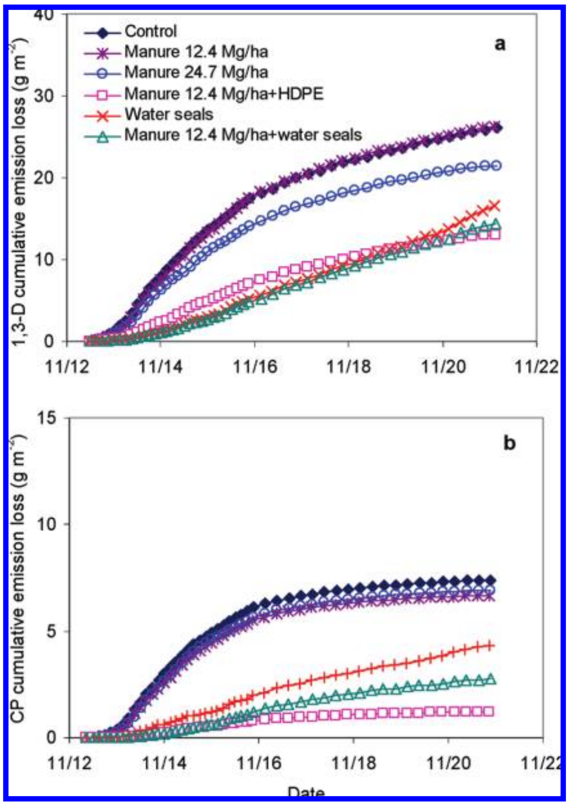

Figure 2. Cumulative emission loss of (a) 1,3-D and (b) CP from manure amendment and water application treatments. Plotted data are averages of three replicates (significant differences between treatments are indicated in **Table 1**). Manure, composted manure; HDPE, high-density polyethylene.

was highest) some flow meters indicated zero flow when other test flow meters indicated that there was actual air flow. The complexity of the chamber design and air flow path made it difficult to estimate the exact flow in the field. The overall impact of artificially low sampling flow recordings could have contributed to the overestimated emission calculations. Estimated corrections for the measured emission losses were 20−40% less. This would place the 80% of emission loss to 60% or less for the control, more comparable with results from other studies. For these reasons, we chose to report the cumulative emission loss in g m^{-2} as the measured value without corrections. These data are more suitable for comparisons of relative differences between treatment effects on emissions.

The cumulative emission loss for 1,3-D was highest for the control and manure amendment at 12.4 Mg ha^{-1}, followed by the manure amendment at 24.7 Mg ha^{-1} (**Table 1**). The cumulative emission loss for the two water seal treatments (i.e., with or without manure application) and the manure + HDPE treatment was about half that of the control. The control and the low rate of manure (12.4 Mg ha^{-1}) amendment resulted in significantly higher total emission loss than the HDPE-tarped manure treatment and the two water (seals) treatments. The total emission loss of 1,3-D from the high rate of manure (24.7 Mg ha^{-1}) fell in between but was not significantly different from any other treatments. The results indicate that a higher rate of manure application may be required to effectively reduce emissions. For CP, the cumulative emission loss from the manure + HDPE treatment was the lowest, significantly lower than all other treatments, except the manure + water treatment.

The steady increase in cumulative emission loss for the two water seal treatments (with and without manure amendment) (**Figure 2**) likely resulted from the relatively constant emission flux throughout most of the monitoring period (**Figure 1**). The high surface soil water content in the water seal treatments could significantly inhibit fumigant transport through the soil surface to reduce emissions. On the other hand, high surface soil water content may have also retained fumigants in soils including those dissolved in the liquid phase, which provided the continuous source for emissions. Increasing soil moisture alone from 5% (w/w) to 15 or 18% had little effect on 1,3-D degradation in batch incubation experiments (*22*). Guo et al. (*23*) showed that hydrolysis of 1,3-D was generally slow with a half-life ranging from 9.3 to 10.1 days from aqueous solutions including water, soil extracts, and suspensions. High fumigation rates can also inhibit microbial activity and reduce microbial degradation of fumigants. These factors may have contributed to the observed trends in this field trial. Other field studies indicate that water seals may or may not significantly reduce cumulative emission loss of 1,3-D depending upon study conditions (e.g., soil moisture and temperature) (*11*, *13*), but it is clear that water seals reduce peak emission flux significantly following fumigation. This field trial illustrated similar findings that water seals reduced emission peak flux (80% reduction) more effectively than cumulative emission loss (50% reduction). Reducing peak flux is important for minimizing potential acute exposure risk for workers and bystanders.

The emission data indicate that manure application at rates of 12.4 and 24.7 Mg ha^{-1} did not significantly reduce emissions during this trial. Postfumigation water applications effectively reduced emission more than the manure treatments, at least within the first few days following fumigation. The role of manure in reducing emissions is that the organic materials can enhance degradation of fumigants both biologically (enhancing microbial activity) and chemically (*22*, *24*, *9*). There may also be reversible and irreversible sorption processes with organic materials that can reduce emissions (*25*). These processes may have resulted in the slightly lower cumulative 1,3-D emission loss from

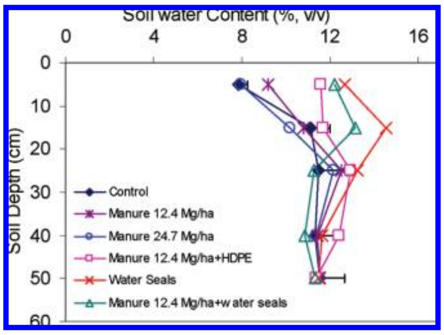

Figure 3. Soil water content measured at the end of the trial. The field capacity is 26% (v/v). Plotted data are averages of three replicates. Manure, composted manure; HDPE, high-density polyethylene.

24.7 Mg h^{-1} compared to the control and 12.4 Mg h^{-1} (**Figure 1**), but these differences were not significant because of the large field variability that increased over time.

The manure (12.4 Mg ha^{-1}) + HDPE treatment was also tested in a previous field trial conducted in 2006 on the same soil, but no emission reduction compared to the control was observed in that trial (*11*). The differences between the two field trials were that, in the 2006 trial, the manure was not incorporated into the soil, the surface soil water content was lower [5.4% in 2006 versus 7.6% (v/v) in this trial], and temperature was higher (average maximum air temperature of 25.4 versus 18.7 °C). These conditions likely contributed to the differences in emission results because several important factors must be considered simultaneously to achieve low emission from soil fumigation.

Soil Water Content, Residual Fumigant, and Temperature. Water content from soil samples taken 14 days after fumigation is shown in **Figure 3**. Irrigation increased soil water content mostly in the 20 cm surface soil. Water seal treatments (with or without manure amendment) resulted in significantly higher (α = 0.05) surface (0−20 cm) soil water content (12.2−12.7%, v/v) than the control and manure amendment treatments (7.8−9.2, v/v). The manure + HDPE treatment resulted in an average soil water content of 9.2% (v/v), which is not significantly different from any other treatments. Prior to fumigation, soil water content of the surface soils averaged 12% (v/v), and it decreased about 3−4% from evaporation loss and seepage when no additional irrigation or tarping was applied. The additional irrigation maintained higher soil water content in surface soils, which reduced emission significantly during the first few days (**Figure 1**); however, reductions for cumulative emission losses are less (**Figure 2**).

Residual fumigants extracted from soil samples at the end of the trial are given in **Figure 4**. The amount of residual fumigants in the soil (liquid + solid phase) followed similar trends as the soil water content; i.e., water seal treatments and the HDPE-tarped treatments had relatively higher fumigant concentrations especially in the surface soils compared to the control and the two manure amendment treatments. Increasing soil water content increases the total portion of fumigants in the aqueous phase compared to the vapor phase. The highest residual fumigant concentrations and the greatest differences among the treatments were observed in the top 30 cm surface soils. The higher residual fumigant concentrations in the water treatments compared to other treatments partially support the continuous emissions observed from these treatments throughout the monitoring period (**Figure 1**). Average concentrations in the soil profiles were analyzed statistically. The manure + HDPE and the two water seal treatments had significantly higher concentrations (ranging from 1.1 to 1.2 mg kg^{-1}) than the control and the two rates of

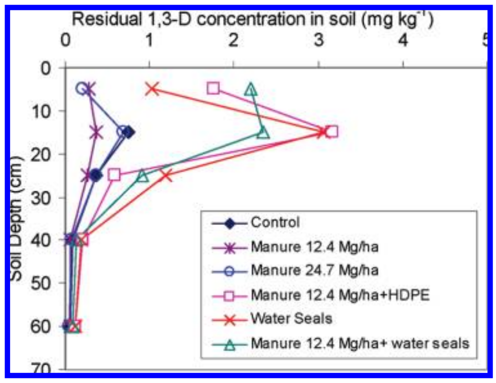

Figure 4. Residual 1,3-D and CP extracted from soil samples 10 days after fumigant injection. Plotted data are averages of three replicates. Manure, composted manure; HDPE, high-density polyethylene.

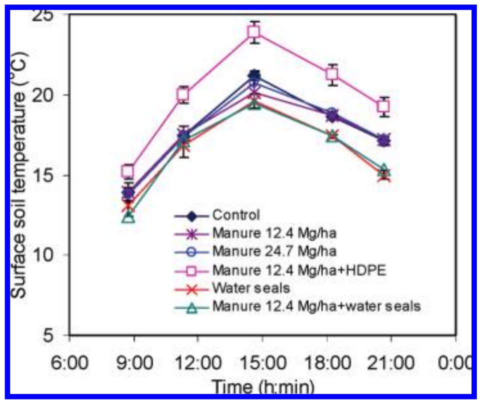

Figure 5. Soil temperature measured at 10 cm depth on October 5, 2007, during the field trial. Error bars are standard deviations of the mean (n = 3). Manure, composted steer manure; HDPE, high-density polyethylene.

manure treatment (ranging from 0.2 to 0.3 mg kg^{-1}). The data indicate that water seals and the manure amendment under HDPE tarp could result in a longer residence time of fumigants in the soil. Thus, the waiting time between fumigation and planting may need to be longer to prevent phytotoxicity to the crop. Residual CP concentrations in the soil were extremely low ($<$0.02 mg kg^{-1}) for all treatments because of much faster dissipation or degradation rates compared to 1,3-D.

Soil temperature measured near the soil surface was the highest in the HDPE-tarped treatment (**Figure 5**). The water seal treatments resulted in the lowest soil temperature. At the lower temperature, the fumigant diffusion rate was reduced leading to low emissions; however, the fumigant degradation rate is also temperature-dependent and could be reduced as indicated by the higher residual fumigant extracted from soils (**Figure 4**). Emission resulting from a surface treatment in the field is the net effect of simultaneous changes or balance of several factors (e.g., moisture and temperature) that affect both the degradation and diffusion of fumigant in soil. A better understanding and information processing in this area using a modeling approach is needed.

Fumigant in Soil Gas Phase. Information about the distribution of 1,3-D in the soil gas phase is given in **Figure 6**. CP (data not shown) followed similar patterns as 1,3-D, except at lower concentration levels because CP dissipates more rapidly than 1,3-D from soils. The half-life of CP was much shorter than 1,3-D (e.g., 1.3 versus 6.3 days in a sandy loam soil) (*22*, *26*). As a result, shortly following fumigant application, the CP concentration was high, with a ratio close to the application ratio, about 57% of 1,3-D. When the fumigant concentration decreased over time, this ratio decreased dramatically to as low as a few percentages of 1,3-D.

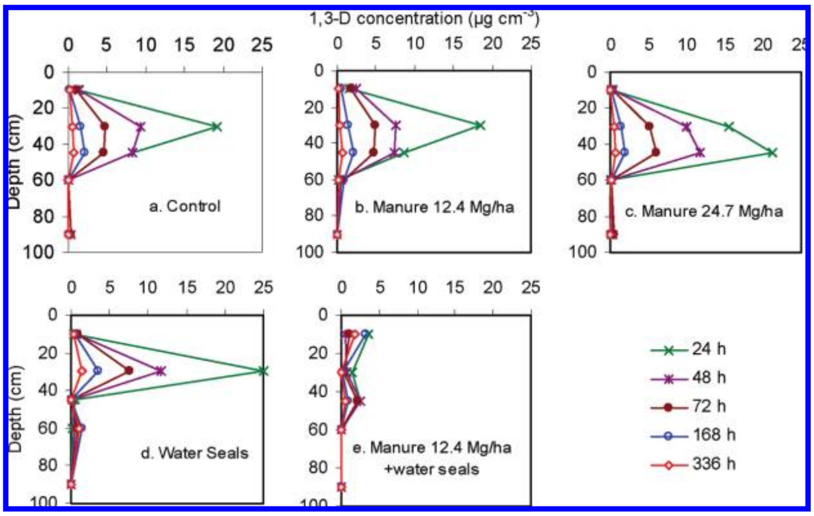

Figure 6. 1,3-D concentration in the soil gas phase at the location adjacent to the fumigant injection line. Manure, composted manure.

A difference in fumigant distribution was observed between sampling locations in the first day or two for all treatments, i.e., higher fumigant concentrations at location a, adjacent to fumigant injection lines, than location b, between injection lines (data not shown). The least difference was observed from the bare soil control treatment. The differences between locations decreased over time. The highest concentrations of 1,3-D (20−25 μg cm^{-3}) at location a were observed within 12 h and 24−48 h at location b. At location a, fumigant concentrations were similar by 24 h among all surface treatments, except the manure + water seal treatment, which had much lower concentrations. Because there was no replicate measurement at the soil gas sampling locations for each treatment, it was uncertain if the much lower soil gaseous fumigant concentration in the manure + water seal treatment was due to the addition of manure and water or potential problems with sampling probes. The manure + HDPE treatment was not monitored for soil gaseous fumigants because an earlier field trial indicated no difference from the control (*11*).

Manure incorporation at the rates of 12.4 and 24.8 Mg ha^{-1} did not adequately reduce fumigant emissions in this field trial. This is contradictory to the conclusions from laboratory experiments showing that organic amendment to soils effectively degraded fumigants and reduced emissions (*7*−*9*) as well as a field test using higher amendment rates (*10*). In laboratory studies, the organic materials were mixed well with homogenized surface soils, and these conditions would be difficult to achieve in the field. Most laboratory-based tests used higher manure application rates [e.g., 5% (w/w) manure in the surface 5 cm soil]; however, achieving this concentration in the field would likely require at least 50 Mg ha^{-1} or higher because field equipment (e.g., chisel or disk) tends to mix soils 10−15 cm deep. Dungan et al. (*10*) reported that higher amendment rates with composted steer and chicken manure at 33 and 65 Mg ha^{-1}, respectively, to surface (5 cm) soil effectively reduced emissions from drip-applied emulsified formulation of 1,3-D in raised beds. The cumulative emission loss of 1,3-D over 170 h was 48 and 28% lower in the steer and chicken manure amended beds, respectively, than the unamended beds, although there was no significant difference between the two application rates for both materials. This information indicates that source materials and application rates may largely determine their effectiveness on fumigant emission reductions. As a soil amendment material, composted manure is used mostly below 25 Mg ha^{-1} in conventional farm lands. Much higher incorporation rates (i.e., $>$25 Mg ha^{-1}) may be needed to achieve effective emission reductions. Better characterization of organic materials is needed in future studies. Higher composted manure application rates may be associated with higher costs unless growers have access to free materials. An application of 25 Mg ha^{-1} (10 tons per acre) would cost roughly \$250−800 ha^{-1} (100−300 per acre) considering delivery and material cost and potentially more depending upon delivery distance from the source.

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