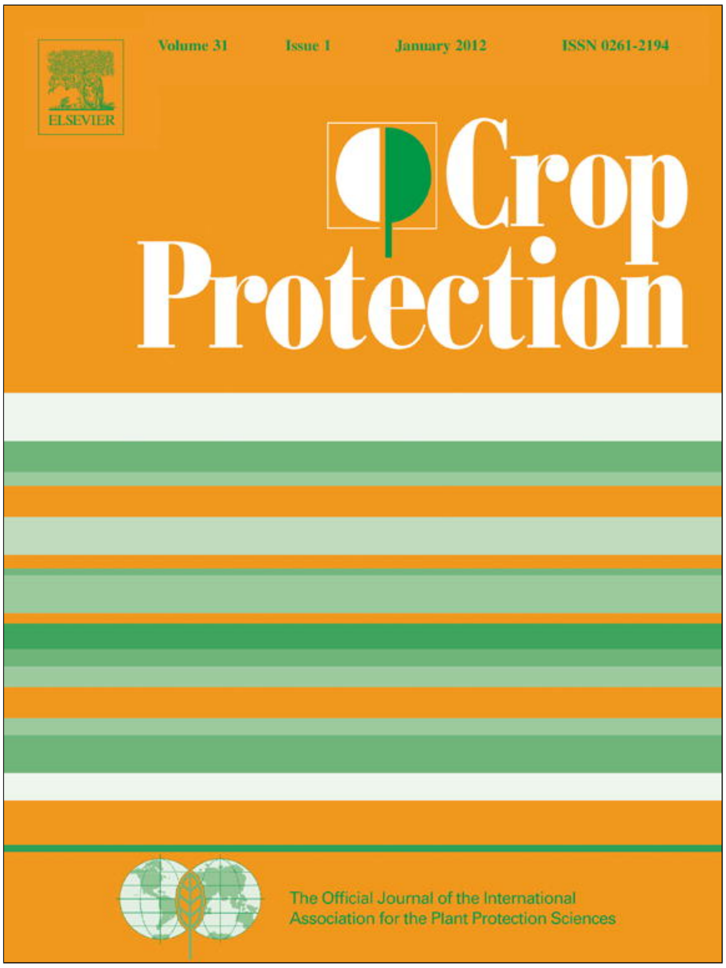
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Fumigant persistence and emission from soil under multiple field application scenarios

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ABSTRACT

Chemical fumigants are routinely used for soil disinfestation of high value crops. Good agricultural practices (GAPs) are needed to reduce their human health risks, environmental impacts, and improve their cost-effectiveness. This study investigated the effect of fumigant application methods on soil persistence and emission of 1,3-dichloropropene (1,3-D) and chloropicrin (CP). Field experiments were conducted to measure the individual and combined effects of pre-application tillage practices, fumigant application technology, and plastic films on 1,3-D soil concentrations to obtain a numerical index (*CT* value) to estimate their potential for pest control efficacy and to compare soil persistence, atmospheric flux rate, and cumulative emission of CP and 1,3-D under two diverse application scenarios. Greater 1,3-D soil vapor concentrations were observed by combining a pre-application soil seal with low soil disturbance application technology when compared to pre-application soil tillage and the use of back-swept application shanks. Under high density polyethylene plastic, the low disturbance scenario resulted in time weighted exposure concentration (*CT*) values ranging from 6.8 to 12.2 μg h cm^{-3} of soil as compared to *CT* values ranging from 2.9 to 5.4 μg h cm^{-3} under the conventional application scenario. Cumulative atmospheric emission of 1,3-D was decreased by 18% under the low disturbance scenario and atmospheric emission of CP by 21% when compared to a conventional application scenario. This study identified GAPs that can be readily implemented in the field to reduce the human and environmental impacts of soil fumigants and improve their cost-effectiveness under solid-tarp (broadcast) applications.

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1. Introduction

Agricultural fumigants are considered critical for control of soilborne pests in high value crop production systems of the United States (Geraldson, 1975; Wilhelm and Paulus, 1980). An impending phase-out of methyl bromide (MeBr) has led to increased use of alternative fumigants including 1,3-dichloropropene (1,3-D) and chloropicrin (CP). In ‘raised bed-plastic mulched’ crop production systems, fumigant combinations involving 1,3-D and CP can achieve pest control levels and marketable yields comparable to methyl bromide when good agricultural practices (GAPs) are followed during the application process (Ajwa et al., 2002; Chellemi and Mirusso, 2004, 2006; Gilreath et al., 1999, 2004; Locascio et al., 1997; Noling et al., 2010). In addition to improving fumigant efficacy, GAPs can extend the soil retention time of fumigants reducing their subsequent atmospheric emission (Chellemi et al., 2010). Key features of GAPs include reduced rate application technologies, improved plastic mulches, emission reduction technology, and optimization of soil environmental and edaphic conditions including moisture and compaction.

Soil porosity and the continuity of pore space are important factors affecting the movement of fumigants (Goring, 1962; Kolbezen et al., 1974; Lembright, 1990). A key feature of raised bed-plastic mulch cropping systems that promotes fumigant retention in soil is the compaction of soil into raised planting beds during the application process. Conversely, in broadcast (solid-tarp) applications, where the fumigant is applied to flat ground and covered with panels of high density polyethylene plastic glued together to

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Abbreviations: CP, chloropicrin; *CT*, time weighted exposure concentration; GAP, good agricultural practices; HDPE, high density polyethylene; PID, photo-ionization detector; VIF, virtually impermeable film; VOC, volatile organic compound; 1,3-D, 1,3-dichloropropene.

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form a solid tarp, a surface tillage is typically performed prior to application to facilitate movement of the injection shanks through the soil profile and to facilitate fumigant dispersion when compaction or high clay levels are present. An unintended consequence of this process is the formation of vertical fissures or grooves in the soil profile as the shanks are dragged through the soil, facilitating transport of soil fumigants to the soil surface. A review of CP fumigant studies found that peak CP flux rates are lower under bedded shank applications than under broadcast applications at the same shank depth (Stanghellini et al., 2010).

Low soil disturbance application technology was first developed to minimize volatilization and grass contamination during the injection of liquid manure in grassland (Chen et al., 2001). The use of vertical coulters placed in front of narrow injection shanks to minimize disruption of the soil surface has been adapted for the application of soil fumigants and studies have indicated they can improve the efficacy of 1,3-D and CP (Dow AgroSciences, 2006; Gilreath et al., 2006; Hochmuth et al., 2004). However, quantitative assessment of their effects on retention of fumigants in soil and subsequent atmospheric emission are lacking under solid-tarp application scenarios. The objectives of the study were to: 1) measure the effects of soil preparation, fumigant application technology, and plastic film on 1,3-D concentrations in soil; 2) obtain a numerical index (*CT* value) to estimate their potential pest control efficacy; and, 3) compare soil persistence, flux rate, and cumulative emission of CP and 1,3-D under a conventional and low disturbance application scenario. Field experiments were conducted in association with the USDA-ARS Area-Wide Pest Management Project for Alternatives to Methyl Bromide (Chellemi and Browne, 2006).

2. Materials and methods

Experiments were conducted on a commercial sod farm in St. Lucie County, Florida, U.S.A. The soil type was a Nettles sand (sandy, siliceous, hypothermic, ortstein, Alfic, Arenic Haplaquods) with 0–2% slope and a spodic horizon at 25–40 cm deep. Soil preparation was typical for fumigated agricultural production fields in the area. Experiments measuring the effect of soil preparation, application equipment, plastic film types on soil concentration of 1,3-D were conducted on 21 March 2008 and on 4 December 2008. A field experiment to quantify soil persistence, flux rate, and atmospheric emission of CP and 1,3-D under two application scenarios was conducted on 17 November 2009.

Soil chemical and physical parameters at application were documented by collecting 8 samples along a diagonal transect line bisecting each treated area. Samples consisted of 5 cores (15 cm × 2 cm) bulked together. Soil bulk density was determined using the core method (Blake and Hartge, 1986). Soil moisture was determined gravimetrically (Gardener, 1986). Water content at field capacity (−0.03 MPa pressure) was determined using ceramic pressure plate moisture extractors (Soil Moisture Equipment Corp., Santa Barbara, CA). Soil texture was determined by the Bouyoucos Hydrometer Method (Bouyoucos, 1936) Soil organic matter was determined by the dichromate reduction method (Walkley and Black, 1934). Soil structure and profile discrepancies, such as plow pans, presence of clods, stones, and crop residue were recorded in the field.

2.1. Fumigant application methods

Soil preparation consisted of surface tillage or a surface seal. Surface tillage was performed using a field cultivator equipped with rolling basket attachments. A surface seal was implemented with a single drum smooth roller. Application technology included conventional back-swept shanks spaced 30 cm apart and 20 cm deep with a fumigant delivery tube welded to the back of the shank and a low disturbance implement. The low disturbance implement was comprised of 0.75 m diameter vertical coulters, spaced 30 cm apart, with steel tubes behind the coulter to deliver fumigants to a 20 cm depth. A 5 cm horizontal steel wing was welded to the delivery tube above the injection point to promote lateral diffusion of the fumigants and a spring-loaded Teflon™ press pan was used to seal the soil surface above the injection points. Plastic film types included a 25 μm thick, clear, high density polyethylene plastic (HDPE, Cadillac Produces, distributed by TriCal, Inc., Hollister, CA) and a 25 μm thick, clear, virtually impermeable film (VIF, Bromostop, Industria Plastica Monregalese, Mondovi, Italy). Samples of each plastic film were collected prior to- and after application and their resistance to fumigant diffusion was determined (Scott Yates, USDA-ARS U.S. Salinity Laboratory in Riverside CA). Details of the procedures of the static chamber procedure are provided elsewhere by Papiernik et al. (2001, 2002). An analytical model was fitted to the data to obtain the mass diffusion coefficient (h). The resistance to diffusion (R) was calculated as the inverse of h following procedures outlined by Papiernik et al. (2010). For the HDPE, R values of 0.2 and 0.1 cm h^{-1} were obtained from cis and trans 1,3-D, respectively. For the VIF, R values of 526 and 208 cm h^{-1} were obtained from cis and trans 1,3-D, respectively.

For the 21 March 2008 and 4 December 2008 application methods study, a factorial design was employed to examine the individual and combined effect of soil preparation, application technology and plastic film. Treatment combinations were replicated 5 times and arranged in a randomized complete block design. Replicate plot were 3 m wide and 30 m long. The fumigant 1,3-D (Dow AgroSciences, Midland, MI, USA) was applied at 226 kg ha^{-1}.

For the 17 November 2009 flux study, two application scenarios were implemented. A conventional scenario consisted of field cultivation followed by fumigant application with back-swept shanks. A low disturbance scenario consisted of a soil surface seal followed by fumigant application using the low disturbance apparatus. Both application combinations were covered by HDPE immediately after application by gluing together panels every 3 m to form a solid tarp. Each application site measured 36 m by 54 m (0.2 ha) and was separated by 600 m. This configuration is considered sufficient in scope and scale for the determination of fumigant flux rates using the Integrated Horizontal Flux Method (Sullivan, D.A., and Ajwa, H.A., 2010). A 60:40 mixture of 1,3-D and CP (Pic-Clor 60, Cardinal Professional Products, Hollister, CA) was applied to both fields. Fumigant cylinders were weighed before and after application on certified scales to facilitate calculation of fumigant mass balance and emission rates. Application rates were 441 kg ha^{-1} for the soil seal-low disturbance combination and 420 kg ha^{-1} for the cultivation-back swept shank combination. Applications were made between 8:00 and 9:00 AM for the low disturbance method and between 10:00 and 11:00 AM for the conventional method.

2.2. Measurement of 1,3-D and CP in soil and soil vapor

A hand-held photoionization detector (PID) (MiniRae 2000, Rae Systems, San Jose, CA) was used to measure 1,3-D soil vapor concentrations in the 21 March and 4 December 2008 methods experiments. The primary use of a PID is to generate real-time quantitative measurements of organic vapors when the identity of the compound is known and its ionization potential is near to or less than that of the ionizing lamp (USEPA, 1994). The PID was used in the 21 March and 4 December 2008 field experiments where only 1,3-D was applied. The PID was not used in the 17 November 2009 flux study, where a mixture of 1,3-D and CP was applied, because the ionization potential of CP (11.42 eV) exceeded that of the 10.6 eV lamp in the PID. Calibration curves were generated before each use with known concentrations of isobutylene at 0, 0.12, 0.24, 0.48 and 1.2 mg L^{-1} (0, 50, 100, 200, and 500 ppm, respectively) and a 0.96 correction factor for 1.3-D was applied to PID readings to permit the expression of 1,3-D concentrations in μg cm^{-3} (RAE Systems, 2006). Air samples were collected by creating a 12 cm deep by 1 cm wide hole through the plastic with a wooden dowel, rapidly inserting the PID air intake into the hole and sealing the sides of the hole so that additional fumigant could not escape. Measurements were taken from replicate plots at 5, 10, and 15 days after application in the March 2008 study and 4, 8 and 14 days after application in the December 2008 study. Samples were collected between 9:00 and 11:00 AM. The averages of 3 measurements were used for each replicate plot.

The concentration of 1,3-D and CP were also determined by drawing a 500 ml air sample through XAD-4 sorbent tubes (SKC 226-175, Eighty-Four, PA) using a personal monitoring pump (SKC Model222). Air samples were collected from a 12 cm by 1 cm hole using the same procedures as for the PID sampling. The pump factor was determined before sample collection by setting the flow rate to 100 ml min^{-1}, determining the number of pump counts per min, and calculating as: Pump factor (ml $count^{-1}$) = (100 ml min^{-1}/number of counts min^{-1}). In the 21 March and 4 December 2008 methods experiments, air samples were collected from the soil cultivation-conventional back-swept shanks-HDPE (conventional) treatment combination and from the surface seal-low disturbance application-HDPE (low disturbance) treatment combination and used for comparison with measurements obtained the handheld PID. In the 17 November 2009 flux study, five air samples were collected from within each flux study location. After collection, sorbent tubes were sealed with plastic caps, placed on ice for transfer back to the laboratory and stored at −20 °C.

For analysis, each section of the XAD-4 tube was extruded into a screw cap vial: a 15 ml vial for the front portion and 4 ml for the rear section. The fiberglass plug at the front of the front section and the polyurethane plug separating the two sections were added to the 15 ml vial. The fiberglass plug at the rear of the XAD-4 tube was added to the 4 ml vial. A combination of 9.8 ml of a 1,2-dichlorobenzene (DCB, 14 mg L^{-1}) in ethyl acetate (EtOAc) solution, 100 μl of MeI-d3 in EtOAc solution and 100 μl of 1-bromo-4-fluorobenzene (BFB) in EtOAc solution were added to the sorbent in the 15 ml vials. In the 4 ml vials, 2.94 ml, 30 μl and 30 μl of the same solutions were added. In each case the BFB served as a surrogate standard, while MiI-d3 served as the internal standard for compounds eluting before the solvent and DCB served as the internal standard for compounds eluting after the solvent. Vials were capped, allowed to desorb for 2 h, and 1 ml was transferred to a 2 ml crimp-top autosampler vial for analysis as described below. The rear section of the tube showing the highest concentration of analyte in the batch was analyzed to check for breakthrough. If there was no breakthrough, none of the other rear sections were analyzed. If breakthrough was <10% of the analyte found in the front portion, the amounts were added together and reported as one. If the amount found in the back section was >10% of the front section, the results were added and flagged, noting that the reported concentration must be considered as a minimum value. Analytical standards for 1,3-D, and CP were purchased from Sigma–Aldrich (St. Louis, MO). EtOAc (OmniSolv grade) was purchased from EMD Chemicals (Gibbstown, NJ).

Soil samples were collected adjacent to the XAD-4 samples by transferring approximately 5 g of soil into 40 ml vials using a "T-bar" sampling device (Environmental Express, Mount Pleasant, SC). Soil samples (5 g) were collected separately at 2 and 10 cm depths. A 10 ml solution of EtOAc containing DCB (14 mg L^{-1}) was immediately added to the vial. Vials were sealed, placed in ice for transport, and stored at −20 °C until analysis. Prior to analysis, vials were reweighed and the masses of the solvent and tare subtracted to yield the accurate mass of the soil sample. The analytical method was developed using a ThermoElectron DSQII quadrupole mass spectrometer equipped with a ThermoElectron trace GC and an AS3000 autosampler. A 25 m × 0.25 mm × 0.25 μ film DB5 FSOT column with UHP helium carrier gas and an electronically controlled volume flow of 1.0 ml min^{-1} with vacuum compensation was used. Samples were introduced into the system using a split injection (20:1 ratio) into a 180 °C injector port. The GC oven was held at 30 °C for 4 min, then increased to 50 °C at 4 °C min^{-1} and finally increased to 120 °C and held there for one minute. The mass spectrometer data collection program had 3 segments. The first segment started at 0.1 min and scanned from m/z 35–160 until 2.4 min into the analysis. The second turned off the MS until the solvent eluted. The third segment scanned from m/z 40–200 until the end of the run. Compound identification was accomplished by comparing the retention times and full scan mass spectra with those measured in the calibration standards. Quantification of the analytes was accomplished by comparing the peak area of extracted ion current profiles in the samples with those in the calibration standards.

2.3. Meteorological data collection

Meteorological data was collected during the November 2009 flux study to facilitate permit the calculation of fumigant flux rates. Two 2D sonic anemometer profile wind systems were established at 0.3, 0.9, 1.8, and 3.0 m above ground level in both application scenarios. A 3D sonic anemometer was placed 3.0 m above ground level to document turbulence. The 3D system also has a very low threshold (<0.002 m s^{-1}) in the event of extremely low wind flow. Standard cup and vane meteorological monitoring systems were installed in each site to document wind flow at approximately 3 m and to measure ambient temperature, relative humidity, solar radiation, and precipitation. Sensor orientation was based upon a Trimble FPS orientation marker. The quality of each data set was reviewed on a daily basis. All meteorological instruments were within the recommended calibration frequency per manufacturer's specification. Soil temperatures during application were monitored with a hand held thermometer inserted into bare soil.

2.4. Ambient air sampling

Air sampling pumps (SKC Inc., Eighty four, PA) were calibrated to draw 50 ml min^{-1} of air through XAD-4 sorbent tubes (SKC 226-175, SKC Inc., Eighty four, PA) and 1 l min^{-1} of air through charcoal tubes (SKC 26-09) (Ashworth et al., 2008). Off-site sample pumps were placed in eight directions surrounding the field, with each pump approximately 12.2 m from the edge of the field. The intake heights were set at 1.5 m above ground level. Off-site sampling was initiated 6 h prior to fumigant application and terminated following the application. For air samples collected post-application, sampling masts were placed at the approximate center of each field site shortly after the passage of the application rig. Air sampling tubes were placed along vertical profiles at 0.3, 0.9, 1.8, and 3.0 m. Air sample tubes were collected at 6 h intervals up to 48 h post application. From 48 to 240 h post application, air sample tubes were collected at 12 h intervals. All sample tubes were removed from the pumps and immediately placed on dry ice for storage and transported back to the laboratory where they were stored at −20 °C.

In order to assess the effect of field sample handling, storage, and transport, field spikes were prepared in the Analytical

Laboratory at JRF America (King of Prussia, PA) and used as part of the quality control documentation for this study. Charcoal and XAD-4 sorbent tubes were fortified with known amounts of CP and 1,3-D and air was drawn through the spikes at a similar flow rate and sampling duration as was used for the collection of the field test air monitoring samples. Spikes were prepared in triplicate at loading levels that bracket the levels anticipated for the air samples. Three blanks also were shipped with each set of spikes. Blanks and field spikes were handled, stored, shipped and analyzed in the same manner as the air samples.

Chloropicrin absorbed onto XAD-4 resin was desorbed with hexane and quantified by gas chromatography with an Electron Capture Detector using previously described methods (CDFACAC, 1999a). A seven-point calibration curve of 0.005, 0.05, 0.02, 0.05, 0.2, and 0.5 ŋg μL^{-1} chloropicrin was obtained at the beginning and end of each set of samples. 1,3-dichloropropene absorbed onto activated charcoal was extracted with 10% carbon disulfide in hexane and quantified with a gas chromatograph equipped with a DB-624 capillary column and an electron capture detector (CDFACAC, 1999b). A six-point calibration curve of 0.025, 0.05, 0.01, 0.5, 1.0, and 5.0 μg ml^{-1} was obtained at the beginning and end of each set of samples.

2.5. Statistical analysis

In the 21 March and 4 December 2008 field experiments, 1,3-D soil vapor concentrations obtained from the PID were analyzed as a factorial using a general linear models procedure with ANOVA (STATISTICA, StatSoft, Tulsa, OK) to determine the individual and combined effects from soil preparation procedure, application equipment and plastic film type on soil vapor concentration of 1,3-D. The data was also used to generate curves of fumigant concentration vs. time by fitting a polynomial, inverse first order equation to the data (SigmaPlot, Systat Software Inc., Point Richmond, CA). Time weighted exposure concentrations (*CT* values) were generated from the curves by numerical integration of the area under the curve using the trapezoid rule (Liengme, 2009) and were expressed in units of μg h cm^{-3}.

2.6. Determination of field flux values

The integrated horizontal flux method (Wilson and Shum, 1992) was used to characterize the mass of fumigant emitted to the atmosphere for all sample periods except the first sample period (initiated 12 h prior to fumigant application and terminated 6 h following the application). For the first sample period, the back calculation method was used and the Industrial Source Complex-Short Term Version 3.0 (ISCST3) and the CALPUFF 6.0 models were used to calculate the flux values (Scire et al., 2000; USEPA, 1999). A more detailed description of those methods is described elsewhere (Sullivan and Ajwa, 2010).

3. Results

3.1. Soil properties and environmental conditions

Soils from experimental locations were similar in texture, being comprised predominantly of sand (91.5%–92.0%) with associated clay contents ranging from 2.0% to 2.7% (Table 1). Soils were also similar in bulk density and organic carbon content. While soil organic carbon levels where low, ranging from 1.4% to 2.3%, those levels are typical for Spodosols and Alfisols located in the Florida Everglades Watershed (Vasques et al., 2010). The largest difference in soil organic carbon level was detected in the two November 2009 study sites, where the values ranged from 1.4% to 2.3%. Soil water content from samples collected during fumigant application ranged from 111 g kg^{-1} to 203 g kg^{-1} and exceeded the water holding capability at field capacity (−0.033 MPa water potential) by 70%–186%.

Ambient weather conditions during and after fumigant application were mild with maximum temperatures of 30.1, 24.8, and 24.1 °C recorded during the March 2008, December 2008, and November 2009 study, respectively. Average soil temperatures at a 15 cm depth were 30.1, 23.1, and 24.2 °C in the March 2008, December 2008, and November 2009 study, respectively. Wind speed during applications in 2008 and 2009 ranged from 2.1 to 2.3 m s^{-1}. No precipitation occurred during or immediately following fumigant applications.

3.2. Comparison of 1,3-D soil vapor detection methods

A direct comparison of 1,3-D soil vapor detection methods was possible in two treatment combinations where both methods were deployed adjacent to each other. In the March 2008 study, the handheld PID and the XAD-4 sorbent tubes detected similar quantities of 1,3-D from the soil atmosphere in the treatment combination that included soil tillage prior to application, backswept application shanks, and HDPE (Fig. 1). Similar detection levels were also obtained in the treatment combination that included rolling the soil surface prior to application (soil seal), low disturbance application technology and HDPE except for day 5 samples, in which higher 1,3-D vapor concentrations were detected with the PID. In the December 2008 study, day 4 concentrations of 1,3-D vapors were detected by the PID under both fumigant application scenarios. While similar detection levels were observed in day 8 and 14 under the conventional application scenario, the PID continued to detect higher concentrations than the XAD-4 sorbent tubes under the low disturbance application scenario.

3.3. Effect of application methods on 1,3-D soil and soil vapor concentration

At 5, 10, and 14 days after application, plastic film significantly impacted the soil vapor concentration of 1,3-D in the March 2008

Table 1
Soil properties at the fumigant application sites.

Parameter	March 2008	December 2008	November 2009 Low-disturbance	November 2009 Conventional
Organic carbon, Mg ha^{-1} (%)	40 (1.8%)	35 (1.6%)	50 (2.3%)	32 (1.4%)
Bulk density, g cm^{-3}	1.50	1.45	1.46	1.53
Sand, g kg^{-1}	920	918	915	915
Silt, g kg^{-1}	60	55	64	58
Clay, g kg^{-1}	20	27	21	27
Water content, g kg^{-1}	111	203	146	123
Field capacity, g kg^{-1} (−33 kPa)	65	71	78	70
Water content (% of field capacity)	170%	286%	187%	174%

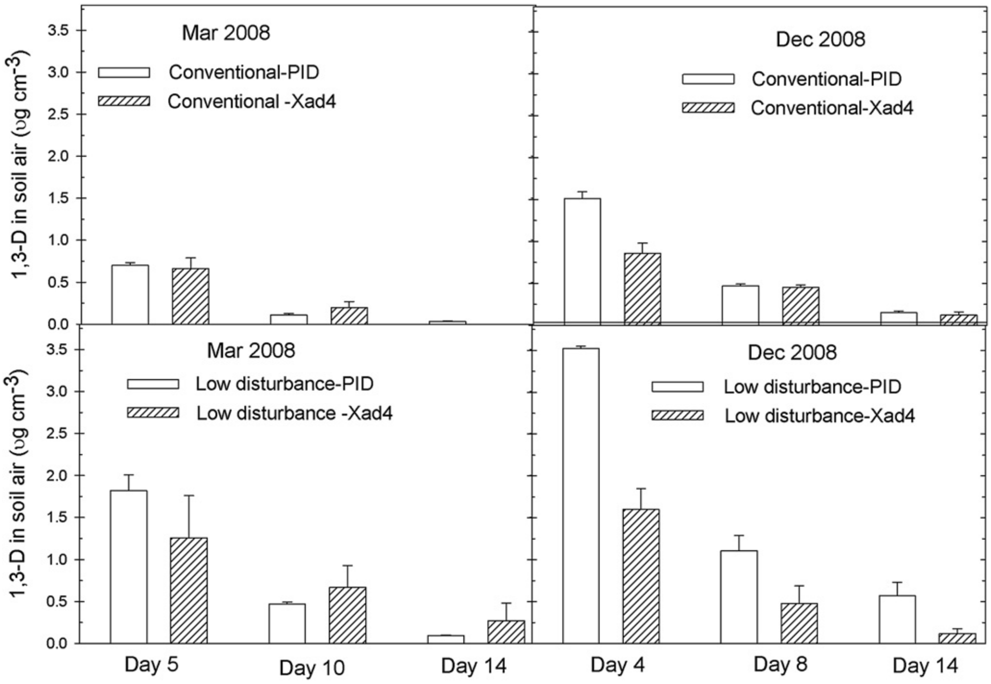

Fig. 1. Comparison of 1,3-D soil vapor concentration measured with a hand-held PID or by drawing an air sample through XAD-4 sorbent tubes. Low disturbance consists of a soil seal, low disturbance application technology and HDPE. Conventional consists of pre-application soil tillage, back-swept shanks, and HDPE.

study (Table 2). Plastic film also impacted 1,3-D soil vapor concentrations in the December 2008 study. In all sample dates, higher 1,3-D soil vapor concentrations occurred under VIF when compared to fumigant applications where HDPE was used to cover the soil.

A significant interaction was observed between soil preparation technique and fumigant application equipment at day 5 in the March 2008 experiment and at days 4 and 8 in the November 2008 experiment. Soil vapor concentrations of 1,3-D were highest when the soil surface was rolled to create a seal and the fumigant application was made with the low disturbance application technology (Fig. 2). Soil vapor concentrations of 1,3-D were lowest when pre-application soil tillage was combined with fumigant application using conventional back-swept shanks. Additional interactions between soil preparation technique, application equipment, and plastic type were not observed in the March and December 2008 studies.

Table 2
Analysis of variance for the effect of application methods on 1,3-D soil vapor concentration.[a]

Application method	Significance level (*P*)		
	Day 5	Day 10	Day 14
March 2008 experiment			
Soil preparation	0.143	0.575	0.896
Equipment	*<0.001*	*<0.001*	*0.913*
Plastic film	*<0.001*	*<0.001*	*<0.001*
Soil preparation × Equipment	*0.026*	0.378	0.496
Equipment × Plastic film	0.310	0.901	0.847
Soil preparation × Plastic film	0.400	0.114	0.475
3-way interaction	0.435	0.633	0.694
December 2008 experiment			
Application method	Day 4	Day 8	Day 14
Soil preparation	*0.028*	0.244	0.364
Equipment	*<0.001*	*0.022*	*0.002*
Plastic film	*0.002*	0.090	0.090
Soil preparation × Equipment	*<0.001*	*0.014*	0.160
Equipment × Plastic film	0.464	0.379	0.487
Soil preparation × Plastic film	0.615	0.372	0.611
3-way interaction	0.684	0.742	0.783

Italics indicate significance at $P < 0.05$.

[a] Measurements obtained with a hand-held PID by drawing air from a 12 cm deep hole created after inserting a wooden dowel through the plastic tarp.

Higher *CT* values occurred in the December 2008 study when compared to *CT* values calculated from the March 2008 study (Table 3). In the March 2008 study, the greatest *CT* value was observed when a surface seal was combined with low disturbance application and VIF (8.16 μg h cm^{-3}). The cultivated-low disturbance-VIF (7.30 μg h cm^{-3}), surface seal-low disturbance-HDPE combination (6.82 μg h cm^{-3}) and cultivated-back swept shank-VIF combination (6.24 μg h cm^{-3}) all displayed *CT* values above 6.00. In the December 2008 study, the same four treatment combinations had the highest *CT* values but the order of ranking differed. The greatest *CT* value was observed in the surface seal-low disturbance-VIF combination (13.66 μg h cm^{-3}) followed by the surface seal-low disturbance-HDPE combination (12.21 μg h cm^{-3}), the cultivated-low disturbance-VIF combination (9.65 μg h cm^{-3}), and the cultivated-conventional shank-VIF combination (8.74 μg h cm^{-3}).

Non-vapor soil concentrations of 1,3-D were also measured in the same treatment combinations where vapor samples were collected with XAD-4 sorbent tubes. In the March 2008 study, non-vapor concentrations near the soil surface (2 cm depth) and the 10 cm depth were higher when a surface seal was combined with low disturbance application equipment (Fig. 3). At day 4 in the December 2008 study, non-vapor concentrations were greater in the treatment combination that included soil surface tillage and back-swept application shanks. At day 8, no differences in non-vapor 1.3-D concentrations were observed between the two treatment combinations. At day 14, non-vapor 1,3-D concentrations were highest under the low disturbance treatment combination at a 10 cm depth.

3.4. Soil vapor and non-vapor concentration of 1,3-D and CP in the November 2009 flux study

Soil vapor concentrations of CP were noticeably higher than the vapor concentration of 1,3-D (Fig. 4). For both fumigants the trend

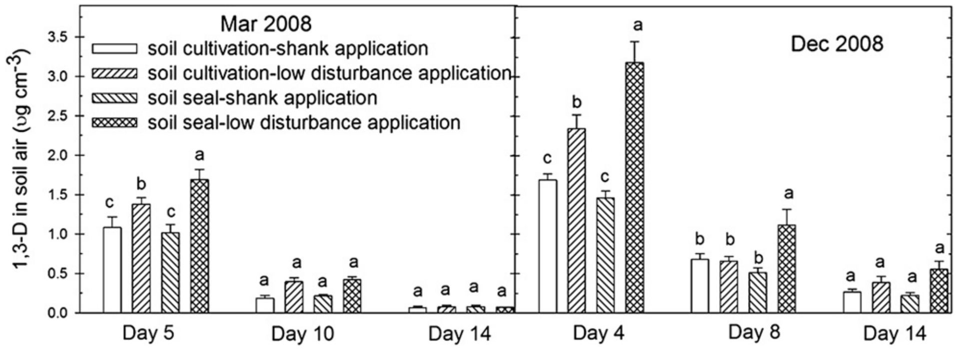

Fig. 2. Combined effect of soil preparation and application equipment on 1,3-D soil vapor concentrations. Treatments covered with HDPE after fumigant application. Fumigant concentrations measured with a handheld PID. Concentrations for each day followed by the same letter are not significantly different according to the Least Significant Difference test ($P < 0.05$).

of concentrations in the soil atmosphere where similar to the results observed in the March 2008 and December 2008 experiments; fumigant concentrations were highest when a surface seal was applied with a roller and applications were made using low disturbance application technology (Fig. 4). Differences in fumigant concentration between the two application scenarios were larger for CP when compared to 1,3-D.

At 2 days after application, soil concentration of 1,3-D at 2 and 10 cm depths were greater under when a surface seal was applied with a roller and applications were made using low disturbance application technology (Fig. 5). This trend continued at 5 and 10 days after application except the magnitude of the difference in non-vapor concentration between the low disturbance and conventional application method was smaller. A different trend was observed for soil (non-vapor) concentrations of CP. At 2 days after application, soil concentrations of CP in the low disturbance and conventional application methods were similar at the 2 cm depth (Fig. 5). At 10 cm, CP soil concentrations were higher with the conventional application method. However, at 5 and 10 days after application, fumigant concentrations in the soil profile were larger in the low disturbance application method, particularly at 10 days after application.

3.5. Emission flux and total emissions of 1,3-D and CP

Fumigant concentrations were not detected in the offsite perimeter air samples collected over a 6-h-period ending immediately prior to their application. Thus, no interference from neighboring agricultural operations was observed for either site. An immediate spike in atmospheric flux of 1,3-D, and CP was observed during the first sample interval (0–6 h after application, Fig. 6). The flux rate of 1,3-D during the first application period was 26.71 and 42.77 μg m^{-2} s^{-1} for the low disturbance and conventional application methods, respectively. For CP, the flux rate during the first 6 h after application was 19.89 and 32.51 μg m^{-2} s^{-1} for the low disturbance and conventional application methods, respectively. Fumigant emission followed a diurnal cycle with peaks in the emissions occurring 3, 27, and 51 h after application. The highest observed flux for 1,3-D was 49.88 and 49.21 μg m^{-2} s^{-1} in the low disturbance and conventional site, respectively. Emission of 1,3-D tapered off significantly after 144 h. The highest observed flux for CP was 46.83 and 46.54 μg m^{-2} s^{-1} in the low disturbance and conventional site, respectively. Emission of CP also declined 144 h after application.

Cumulative atmospheric emissions were calculated from the mass of fumigant applied and the cumulative loss rates measured over the course of the study and are expressed as a percentage of the fumigant applied. Cumulative emission of 1,3-D was 21% greater under the conventional application scenario that included soil surface tillage and back-swept application shanks when compared to the low disturbance application scenario that included a soil seal and low disturbance technology (Fig. 7). Cumulative emission of CP was 18% greater under the conventional application scenario when compared to the low disturbance application scenario.

Table 3
Effect of application methods on the time weighted exposure concentration (*CT*) of 1,3-D in the soil atmosphere.

Method			Experiment	
Soil preparation	Application equipment	Plastic film	March 2008	December 2008
Cultivated	Conventional shank	HDPE	2.87[a]	5.36
Cultivated	Conventional shank	VIF	6.24	8.74
Cultivated	Low disturbance	HDPE	5.44	7.80
Cultivated	Low disturbance	VIF	7.30	9.65
Surface seal	Conventional shank	HDPE	3.38	4.89
Surface seal	Conventional shank	VIF	5.61	6.70
Surface seal	Low disturbance	HDPE	6.82	12.21[b]
Surface seal	Low disturbance	VIF	8.16	13.66[b]

[a] Expressed as μg h cm^{-3}.

[b] Exceeds the threshold value of 12.0 μg h cm^{-3} required for 100% mortality of *Tylenchulus semipenetrans* (Wang and Yates, 1999).

4. Discussion

This study demonstrated the application potential of properly calibrated hand-held PIDs, with supported validation (quality assurance checks) by collecting fumigant vapors onto sorbent collection tubes. The hand-held PID provided reproducible real-time assessment of 1,3-D vapor concentrations in soil following application. In the March 2008 study, side-by-side comparisons to XAD-4 sorbent collection tubes resulted under diverse application scenarios (Fig. 1). Although 1,3-D concentrations detected with the PID where higher than the concentrations obtained by XAD-4 tubes in the December 2008 study, both detection methods identified a trend in decreasing 1,3-D concentrations by ≈50% between each sample date. Use of PIDs can facilitate and expand fumigant detection capability in the field through improved logistics and reduced sampling costs. The hand-held PID also has application potential to address commercial growers concerns regarding residual fumigant residues in soil after application and their subsequent affect on transplanted crops.

Higher 1,3-D soil vapor concentrations under VIF were attributed to an increased resistance to fumigant diffusion (*R*). The VIF

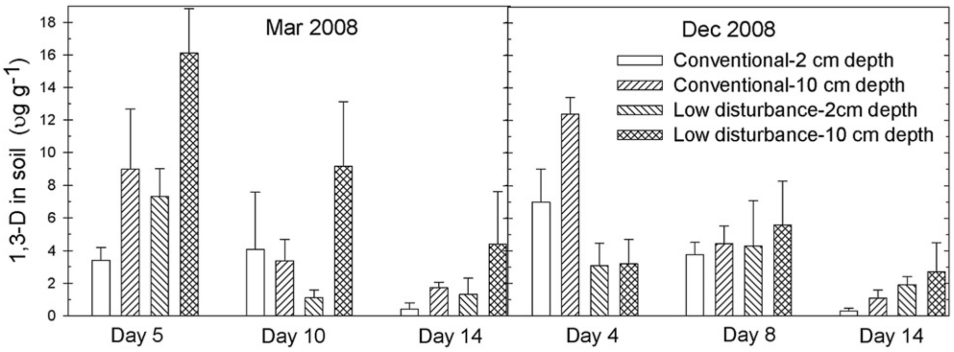

Fig. 3. Non-vapor concentration of 1,3-D at 2 cm and 10 cm soil depths. Low disturbance consists of a soil seal, low disturbance application technology and HDPE. Conventional consists of pre-application soil tillage, back-swept shanks, and HDPE.

had R values of 601, 208, and 9200 h cm^{-1} for 1,3-D (cis), 1,3-D (trans) and CP, respectively. For the HDPE, R values of 0.20, 0.12, and 0.67 h cm^{-1} were associated with 1,3-D (cis), 1,3-D (trans) and CP, respectively. All R values were within the range typically observed for HDPE and VIF (Papiernik et al., 2010). The resistance to the diffusion of 1,3-D was 3 orders of magnitude greater with VIF while resistance to diffusion of CP was 4 orders of magnitude higher, when R values are compared to those observed for HDPE. Handling of VIF during its application in the field reduced permeability to 1,3-D (cis), 1,3-D (trans) and CP by 49%, 42% and 55%, respectively. Despite the increased permeability, VIF remained 2–3 orders of magnitude more resistant to diffusion of 1,3-D and 3 orders of magnitude more resistant to diffusion of CP than HDPE. This behavior was also typical of VIF after field application in raised bed-plastic mulched cropping systems (Papiernik et al., 2010).

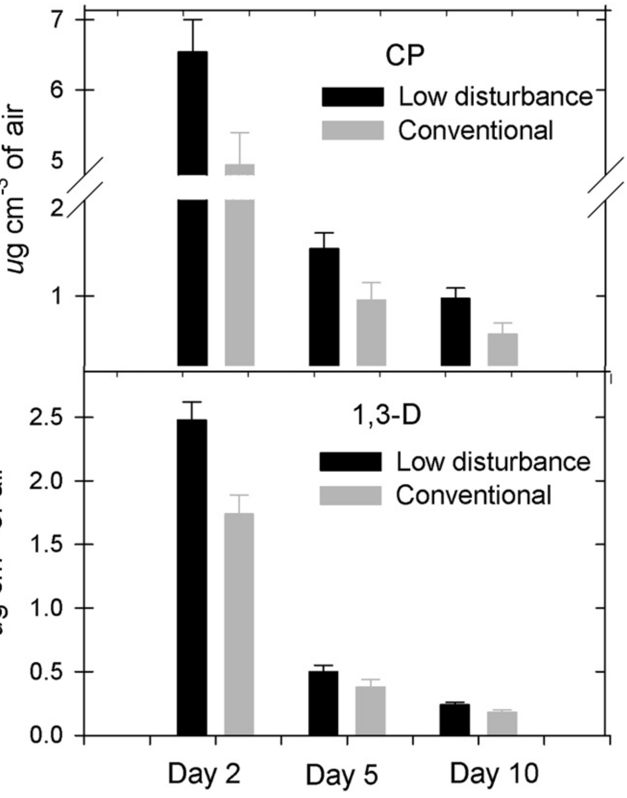

Fig. 4. Soil vapor concentration of CP and 1,3-D in the November 2009 flux studies measured by drawing air samples through XAD-4 sorbent tubes. Low disturbance consists of a soil seal, low disturbance application technology and HDPE. Conventional consists of pre-application soil tillage, back-swept shanks, and HDPE.

Recent studies have focused on reducing fumigant emissions through soil surface seals (Gao et al., 2008, 2011; Thomas et al., 2004; Wang et al., 2005; Zhang and Wang, 2007), drip or deep shank fumigant injection methods (Ajwa et al., 2002; Wang et al., 2001), soil moisture (McDonald et al., 2009; Qin et al., 2009) and organic material (Yates et al., 2011). This study demonstrated the use of low disturbance application technology combined with a soil surface seal to improve retention of soil fumigants. Higher non-vapor concentration of 1,3-D on day 4, December 2008 conventional application (Fig. 3) was attributed to excessively high soil moisture (286% of field capacity) at application. Under the high soil moisture conditions, it is postulated that 1,3-D remained in solution as a dense non-aqueous phase liquid for an extended time period, restricting movement through the soil profile. Field plots were large enough to permit the low disturbance apparatus (0.75 m diameter vertical coulters, spaced 30 cm apart, with steel fumigant delivery tubes behind the coulter, a 5 cm horizontal steel wing welded to the delivery tube above the injection point, and a spring-loaded press pan was used to seal the soil surface above the injection points) to operate as in commercial production operations under representative field conditions.

Extending fumigant retention in soil will directly impact efficacy. First introduced by Busvine (1933), the lethal dose of a toxicant is a function of both time (T) and concentration (C). Applications of this concept to establishing fumigant efficacy thresholds for soilborne fungi (Munnecke and van Gundy, 1979) and plant parasitic nematodes (McKenry and Thomason, 1974) were summarized as a CT, the product of pesticide concentration and time. The CT value is determined as the integral of the fumigant concentration with respect to time. This concept was expanded further by Wang et al. (2004) to account for the ratio between the soil volume where CT exceeded a threshold value for a particular pest-fumigant combination and the total soil volume that was required for fumigant treatment. While useful in understanding the spatial and temporal dynamics of concentration and time, the modified CT index proposed by Wang et al. (2004) was not applied to data in this study because 1,3-D vapor concentrations were collected from a single line source (0–12 cm depth).

CT values are presented as a numeric efficacy index to facilitate the evaluation of the various fumigant application methods. Combining a surface seal with low disturbance applications and HDPE resulting in CT values larger than those obtained by combining VIF with conventional back-swept shank applications and produced the 3rd highest CT value in the March 2008 study and the 2nd highest CT value in the December 2008 study. Furthermore, combining a surface soil seal with low disturbance applications under HDPE produced CT values 2.3–2.4 times larger than the industry standard (surface cultivation, back-swept shank application and HDPE). Relevance of CT values to pest control is obtained

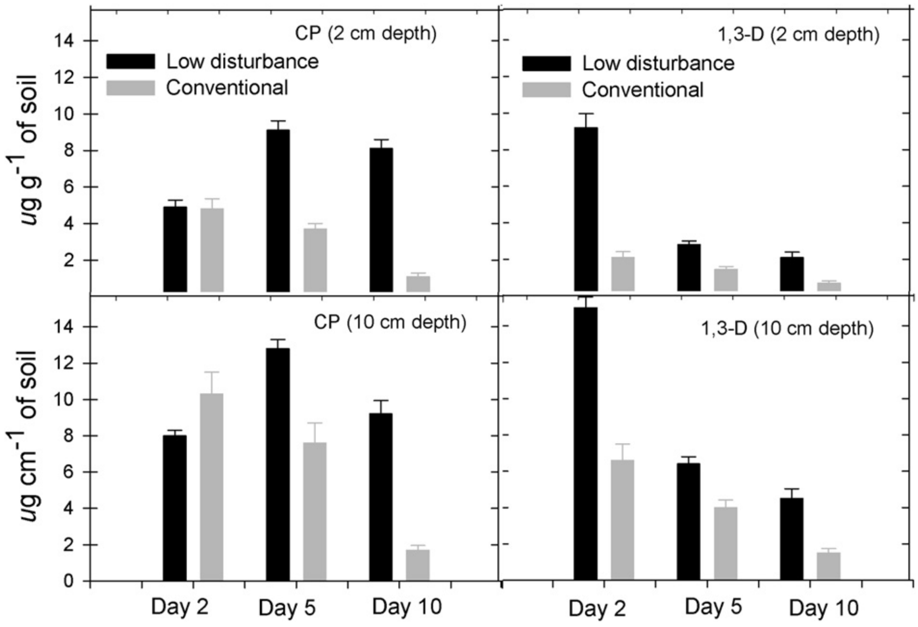

Fig. 5. Non-vapor concentration of CP and 1,3-D in the November 2009 flux studies measured by drawing air samples through XAD-4 sorbent tubes. Low disturbance consists of a soil seal, low disturbance application technology and HDPE. Conventional consists of pre-application soil tillage, back-swept shanks, and HDPE.

by comparison to a threshold *CT* value for 1,3-D of 12 μg h cm^{-3}, required 100% mortality of the citrus nematode (*Tylenchulus semipenetrans*) (Wang and Yates, 1999). Using the 12 μg h cm^{-3} threshold, effective control of citrus nematode would not have been achieved in the March 2008 study. However, the 1,3-D application rate used in this study (226 kg ha^{-1}) was lower than the recommended label rate of 372 kg ha^{-1} for certification of nematode free nursery stock in California (Telone II Product Bulletin, Dow AgroSciences, Indianapolis, IN). Effective *CT* thresholds for citrus nematode were achieved in the December 2008 study in treatments combining a surface soil seal with low disturbance application technology. Thus, *CT* values above the effective control threshold were obtained with a 40% reduction in the quantity of fumigant when applied using the soil seal-low disturbance combination.

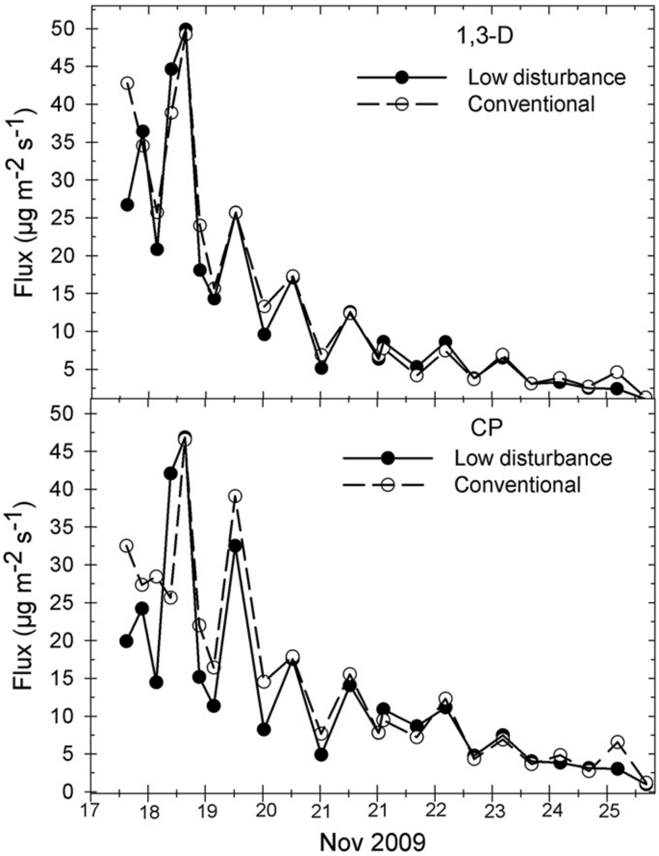

Fig. 6. Atmospheric flux rate of CP and 1,3-D under two application scenarios. Low disturbance consists of a soil seal, low disturbance application technology and HDPE. Conventional consists of pre-application soil tillage, back-swept shanks, and HDPE.

Reports of 1,3-D cumulative atmospheric emission after soil application varies from 11% to 90% (Chellemi et al., 2010; Cryer et al., 2003; Cryer and van Wesenbeeck, 2010; Gao et al., 2008; Qin et al., 2009; McDonald et al., 2009; Wang et al., 2001). For CP, cumulative emissions are generally lower but still vary widely from 2% to 50% (Chellemi et al., 2010; Gao et al., 2008; Qin et al., 2009; Zhang and Wang, 2007). The range of observed atmospheric

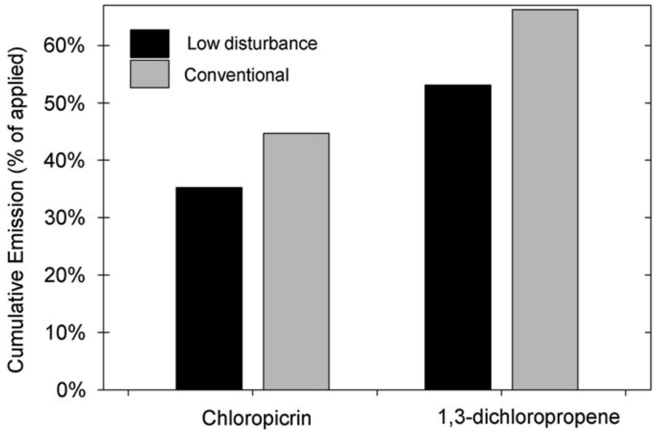

Fig. 7. Total cumulative atmospheric emission expressed as the percent of fumigant applied. Low disturbance consists of a soil seal, low disturbance application technology and HDPE. Conventional consists of pre-application soil tillage, back-swept shanks, and HDPE.

emissions are attributed to a multitude of complicating factors including laboratory vs. field studies, solid tarp vs. bedded application scenarios, differing soil types, organic matter contents, soil water contents, fumigant application depths and the differences in the permeability of plastics to soil fumigants. Thus, it is difficult to directly compare emission values obtained to those in previous studies other than to generalize that 1,3-D and CP emissions were within the range of previously reported values.

This study created an opportunity to examine fumigant flux under field conditions representative of commercial fumigant applications while simultaneously minimizing variability in flux rates due to differences in soil type, environmental, and soil edaphic conditions from site to site. Soil water content at the time of fumigation exceeded the water content at field capacity by >70%–186%, creating near saturated soil conditions. It is common in Florida crop production systems for soil moisture in excess of field capacity to occur during fumigant application (Chellemi et al., 2011). The custom of maintaining high soil moisture for agricultural production in the Florida Everglades Watershed is facilitated by the presence of a perched water table and spodic horizon (hardpan) just below the soil surface. Higher water content reduces subsurface dispersion of 1,3-D and CP and increases their residence time in soil (Cryer and van Wesenbeek, 2010; Gao et al., 2008; Gan et al., 1998; Thomas et al., 2004). Use of a water seal also significantly reduced the cumulative emissions of MITC and CP in Georgia (Wang et al., 2005). Thus, it is likely that the high soil moisture conditions at the time of fumigation facilitated the retention of fumigant in the soil and reduced their atmospheric emission. Despite the presence of high soil moisture, differences in peak flux rates and cumulative atmospheric emission of 1,3-D and CP were observed.

Combining a soil surface seal with low disturbance technology reduced cumulative atmospheric emission of 1,3-D by 21% and CP by 18%. Differences in the maximum flux rate over the 10-day sample period were not observed between the two application scenarios. However, a reduction in the flux rate of CP from 32.5 to 19.9 $\mu g\ m^{-2}\ s^{-1}$ during the sample period immediately following application was observed when the soil surface seal was combined with low disturbance application technology. A similar reduction in the flux rate of 1,3-D during the first 6 h after application from 42.7 to 26.7 $\mu g\ m^{-2}\ s^{-1}$ was also observed for the low disturbance scenario. High flux rates of CP immediately following application have been observed even in raised bed-plastic mulched applications where a VIF was used (Qin et al., 2009). From the perspective of worker protection, any reduction in atmospheric emission of soil fumigant immediately following application is critical as this is the time period when many farm workers are still present in the vicinity of the treated area. Thus, the combined use of a surface soil seal and low disturbance application technology may potentially reduce the risk of exposure to fumigants by workers present in the field during and immediately preceding application.

Increased *CT* values and thus, improved efficacy may be realized by prolonging retention of fumigants in soil, particularly in the vapor phase, and offers the potential to mitigate their environmental impact by reducing the effective application rate. Prolonged soil retention is also associated with reduced atmospheric emission, a critical health and environmental concern regarding soil fumigants. However, prolonged soil retention may increase the possibility for movement of fumigants into surface or ground water, particularly if the fumigant remains as a dense non-aqueous phase liquid within the soil environment. Prolonged soil retention can increase plant back times due to the threat of crop injury from residual fumigants (MacRae et al., 2010). Realizing the benefits of increased fumigant retention in soil should always be weighed against its potential drawbacks and site specific decisions should be made regarding the selection of fumigants, application rates and application methods.

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