Soil Fate of Agricultural Fumigants in Raised-Bed, Plasticulture Systems in the Southeastern United States

Dan O. Chellemi,* Husein A. Ajwa, David A. Sullivan, Rocco Alessandro, James P. Gilreath, and Scott R. Yates

Soil concentrations and degradation rates of methyl isothiocyanate (MITC), chloropicrin (CP), 1,3-dichloropropene (1,3-D), and dimethyl disulfide (DMDS) were determined under fumigant application scenarios representative of commercial raised bed, plastic mulched vegetable production systems. Five days after application, 1,3-D, MITC, and CP were detected at concentrations up to 3.52, 0.72, and 2.45 µg cm^{-3}, respectively, in the soil atmosphere when applications were made in uniformly compacted soils with a water content >200% of field capacity and covered by a virtually impermeable or metalized film. By contrast, DMDS, MITC, and CP concentrations in the soil atmosphere were 0.81, 0.02, and 0.05 µg cm^{-3}, respectively, 5 d after application in soil containing undecomposed plant residue, numerous large (>3 mm) clods, and water content below field capacity and covered by low-density polyethylene. Ranked in order of impact on the persistence of fumigants in soil were soil water content (moisture), soil tilth (the physical condition of soil as related to its fitness as a planting bed), the type of plastic film used to cover fumigated beds, and soil texture. Fumigants were readily detected 13 d after application when applied in uniformly compacted soils with water contents >200% of capacity and covered by a virtually impermeable or metalized film. By contrast, 1,3-D and MITC had dissipated 5 d after application in soils with numerous large (>3 mm) clods and water contents below field capacity that were covered by low-density polyethylene. Soil degradation of CP, DMDS, and MITC were primarily attributed to biological mechanisms, whereas degradation of 1,3-D was attributed principally to abiotic factors. This study demonstrates improved soil retention of agricultural fumigants in application scenarios representative of good agricultural practices.

PREPLANT SOIL FUMIGATION with methyl bromide (MB) is an essential component of high-value vegetable production systems in the United States. Since the 1960s, soil fumigation has been largely credited for the sustained high yields of fresh market pepper, strawberry, and tomato production (Geraldson, 1975; Wilhelm and Paulus, 1980). Traditionally, mixtures of MB and chloropicrin (CP) are shank injected into soil beds as the soil is pressed into planting beds (0.75–0.90 m wide by 15–20 cm high), which are immediately covered with polyethylene plastic film after fumigation (Cantliffe et al., 1995; Olson and Simonne, 2007). The plastic film is left on the raised beds to function as mulch. Recognition of MB as a stratospheric ozone-depleting chemical (Chakrabarti and Bell, 1993) led to the legislatively mandated phase-out of its production and sale in the United States (Clean Air Act, 1990; Federal Register, 1993).

1,3-dichloropropene (1,3-D), CP, and the methyl isothiocyanate (MITC) generators metam potassium and metam sodium are alternative preplant soil fumigants registered for use in the United States for the control of soil-borne pests and diseases of agricultural crops They are labeled as Restricted Use Pesticides by the USEPA due to their high acute toxicity. Dimethyl disulfide (DMDS) is undergoing registration approval. When coapplied using good agricultural practices (GAPs), these fumigants can achieve a spectrum of pest and disease control similar to methyl bromide while maintaining a high level of marketable yields (Ajwa et al., 2002; Chellemi and Mirusso, 2004, 2006; Gilreath et al., 1999; Locascio et al., 1997; Noling and Gilreath, 2000). Good agricultural practices include improved application methods and technology, reduced application rates, and selective inclusion of specific soil edaphic and environmental conditions. In July 2008, the USEPA proposed substantial label changes for CP and MITC generators to mitigate by-stander and occupational (worker) exposure resulting from the application procedures (Federal Register, 2008). As written, the exposure mitigation requirements based on available field-scale flux data would make it extremely difficult, if not impossible, for many growers to apply these fumigants.

D.O. Chellemi and R. Alessandro, USDA–ARS, US Horticultural Research Lab., 2001 S. Rock Road, Fort Pierce, FL 34945; H.A. Ajwa, Dep. of Vegetable Crops, Univ. of California, 1636 East Alisal St., Salinas, CA 93905; D.A. Sullivan, Sullivan Environmental Consulting, Inc. 1900 Elkin St., Suite 200, Alexandria, VA 22308; J.P. Gilreath, PhytoServices, 16 W. Hillcrest Dr., Greenville, SC 29609; S.R. Yates, USDA–ARS, U.S. Salinity Lab., 450 W. Big Springs Rd., Riverside, CA 92507. Assigned to Associate Editor Robert Dungan.

Abbreviations: CP, chloropicrin; DMDS, dimethyl disulfide; 1,3-D, 1,3-dichloropropene; EtOAc, ethyl acetate; GAP, good agricultural practice; GC, gas chromatograph; LDPE, low-density polyethylene; MB, methyl bromide; MITC, methyl isothiocyanate; PID, photoionization detector; VIF, virtually impermeable film; VOC, volatile organic compound.

Previously, studies have been initiated to model fumigant soil flux and atmospheric emissions over large areas using methods and conditions representative of commercial production practices (Cryer and Wesenbeeck, 2009; Li et al., 2006). However, corresponding data documenting the fate of fumigants in soil when applications were made under GAPs are lacking, most notably when applications are made over large areas using methods and conditions representative of commercial production practices. Information pertaining to the dissipation of fumigants in soil is critical for determining the potential environmental risks of off-site infiltration into ground and surface water. Quantifying fumigant persistence in soil under commercial application conditions will facilitate extrapolation of fumigant emissions in the field based on limited sets of initial measured parameters using flux/emission models, such as the PRZM3, CHAIN-2D, and SOFEA models. Generating time-weighted exposure concentrations (CT values) in soil after application will enable fumigant efficacy assessment for a broad spectrum of soil-borne pests and diseases. Prolonged fumigant persistence in soil can significantly extend plant-back intervals, negatively affecting horticultural operations (MacRae et al., 2010).

The goal of this study was to ascertain the effects of application and soil factors on the persistence of fumigants in soil under commercial application scenarios that incorporate GAPs. The specific objectives were to quantify vapor and non-vapor soil concentrations of MITC, CP, 1,3-D, and DMDS under a range of commercial application scenarios representative of raised bed, plastic mulched vegetable production systems in the Southeastern United States and to identify their corresponding rate of degradation in the soil. Data were collected from six field trials affiliated with the USDA-ARS Area-Wide Pest Management Project for Alternatives to Methyl Bromide (Chellemi and Browne, 2006) conducted in Florida and Georgia to ensure representative participation by growers and industry professionals.

Materials and Methods

Site Characterization: Florida Trials

Three field sites were selected on a commercial farm in the Palmetto-Ruskin tomato production region of Florida (Manatee County). Sites were representative of Florida raised bed, plastic mulch vegetable production including a characteristic soil type, typical land preparation, and season for fumigant application. Each 0.4-ha site was in close proximity but separated by a minimum distance of 600 m. Soil type at the three sites was Myakka fine sand (sandy, siliceous, hypothermic Aeric Haplaquods) with 0 to 2% slope and a spodic horizon that is typical for fumigated vegetable production fields in the area. Soil characteristics and conditions at application were determined by collecting eight samples along a transect line that bisected each treated area diagonally. Samples consisted of multiple 15 cm × 2 cm cores. 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 (−0.033 MPa pressure) was determined using ceramic pressure plate moisture extractors (Soil Moisture Equipment Corp., Santa Barbara, CA). Soil texture was deter-

mined 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 and the presence of clods, stones, and crop residue were recorded in the field. A small hole was dug to a depth of 45 cm in two locations across each field, and soil density changes through the profile observed and noted.

Application Scenarios: Florida Trials

In Site 1, a three-way combination of 1,3-D (Telone II; Dow AgroSciences, Midland, MI), CP (Metapicrin; HyYield Bromine, Inc., Plant City, FL), and metam potassium (KPAM; AMVAC Chemical Corp., Los Angeles, CA) was applied under a 30-µm thick, silver metalized film (Canslit Inc., Quebec, Canada). Fumigant applications were made sequentially in rapid succession with the plastic placed onto beds immediately after the final fumigant was applied. Three different implements were used to complete the application procedure. First, 1,3-D and CP were applied through separate lines using back-swept shanks spaced 25 cm apart at 20 cm depths. Behind the application shanks, beds (81 cm wide × 23 cm high) were immediately formed and pressed using a pan attached to the same implement. Second, metam potassium was injected into the pressed beds at a 10-cm depth using 25-cm vertical coulters spaced 10 cm apart across the bed width. Third, beds were pressed again with the second implement and then immediately covered with metalized plastic film using a third implement. The application in Site 2 was identical to the application in Site 1, except that a 30-µm thick virtually impermeable film (VIF) (Guardian; Grupo Olefinas, Villa Nueva, Guatemala) was used to cover the fumigated beds. The application in Site 3 was identical to the application in Site 1, except that the 1,3-D was omitted from the procedure. Applications were made on 14 Jan. 2009. The application in Site 1 took place between 1043 and 1149 h. The application in Site 2 took place between 1322 and 1437 h. The application in Site 3 took place between 1603 and 1651 h. Fumigant cylinders were weighed before and after application on certified scales. The application rates are provided in Table 1.

Site Characterization: Georgia Trials

Three field sites were located on or near the University of Georgia Tifton Research facility. Sites were representative of Georgia raised bed, plastic mulch vegetable production, including a characteristic soil type, typical land preparation, and season for fumigant application. Each 0.4-ha site was in

Table 1. Fumigant application rates at the Florida and Georgia trials.

Fumigant	Site 1	Site 2	Site 3
Florida trials			
1,3-Dichloropropene, kg ha⁻¹	142	145	n/a†
Chloropicrin, kg ha⁻¹	192	198	184
Metam potassium, kg ha⁻¹	348	336	342
Georgia trials			
Dimethyl disulfide, kg ha⁻¹	612	603	637
Chloropicrin, kg ha⁻¹	162	160	169
Metam sodium, kg ha⁻¹	335	343	331

† 1,3-Dichloropropene not applied.

close proximity but separated by a minimum distance of 600 m. The soil type for Sites 1 and 2 was Tifton loamy sand (fine-loamy, kaolinitic, thermic Plinthic Kandiudults). The soil type for Site 3 was a Dothan sandy loam (fine-loamy, kaolinitic, thermic Plinthic Kandiudults). Both soil types are typical for fumigated vegetable production fields in the region. Soil characteristics and conditions at application were characterized using the same previously described procedures.

Application Scenarios: Georgia Trials

In Site 1, a three-way combination of CP (Hendrix & Dail, Tifton, GA), DMDS (Paladin; Arkema Inc., Philadelphia, PA), and metam sodium (VAPAM; AMVAC Chemical Corp., Los Angeles, CA) was applied under black, 30-μm VIF (Blockade; Pliant Corp., Dalton, GA). Fumigant applications were made sequentially in rapid succession with the plastic placed onto beds immediately after the final fumigant was applied. The application used three separate implements. First, DMDS and CP were applied as a pre-bed application using three back-swept shanks spaced 30 cm apart at 20-cm depths. The fumigants were premixed in a cylinder, and a single delivery line was used to carry the mixture to the shank. Behind the application shanks, beds (90 cm wide × 15 cm high) were immediately formed and pressed using a pan attached to the same implement. Second, metam sodium was injected into the pressed beds at a 10-cm depth using 25-cm vertical coulters spaced 10 cm apart across the full bed width. Third, beds were pressed again with the second implement and immediately covered with VIF (Blockade; Pliant Corp.) using a third implement. The application in Site 2 was identical to the application in Site 1, except that black, 25-μm low-density polyethylene (LDPE) (Pliant Corp.) was used to cover the fumigated beds. The application in Site 3 was identical to the application in Site 2, except for a different soil type. All applications were made on 7 Feb. 2009. The application in Site 1 took place between 12:47 and 2:21 PM. The application in Site 2 took place between 3:19 and 4:48 PM. The application in Site 3 took place between 5:40 and 7:57 PM. Fumigant cylinders were weighed before and after application on certified scales. The application rates are provided in Table 1.

Measurement of Plastic Permeability

Samples of the plastic mulches were taken directly from the roll before field application and from the field after application. Field samples were collected from an untreated section to assess the impact of application methods and equipment on plastic permeability to fumigants. Samples were carefully placed in a protective shipping container and expedited to the USDA–ARS U.S. Salinity Laboratory in Riverside, CA, for testing.

Details of the apparatus, procedures, and analysis are given elsewhere (Papiernik et al., 2001, 2002). Permeability was determined in static sealed cells in which fumigant vapor is spiked to one side of the film and the concentrations on both sides of the film are monitored over time, preferably until equilibrium. Samples were analyzed using an HP 6890 gas chromatograph (GC) in tandem with an Agilent 5975 Mass Selective Detector equipped with a HP-5MS column (30 m 0.25 mm i.d., 0.25-μm film thickness; J&W, Folsom, CA). Helium was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. A split injection (10:1 ratio) into a 250°C injector port was used. The initial oven temperature was 50°C. The temperature was increased to 70°C at 3.5°C min^{-1}, then increased to 120°C at 10°C min^{-1}, and held for 1 min. Mass spectrometric analysis was performed using full-scan and selected ion monitoring modes. In the full-scan mode, the electron impact mass spectra were generated using an electron energy of 70 eV, and ions with m/z 45 to 500 were monitored. The full-scan mode was used for the analyte identification by fragmentation patterns. For improved sensitivity, selected ion monitoring was used for quantitation. Quantification was accomplished by comparing the area of the selected ion peak of the analyte of interest with the area of the selected ion peak from the fumigant standards (obtained from Sigma-Aldrich, St. Louis, MO). 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). This model relies on a mass balance approach and includes sorption to and diffusion across the film membrane. All tests were conducted in triplicate in rooms with the temperature controlled to within ±0.5°C. All equipment was equilibrated at the experimental temperature before each experiment was initiated.

Measurement of Volatile Organic Compounds in the Soil Atmosphere

A hand-held photoionization detector (PID) (MiniRae 2000; Rae Systems, San Jose, CA) equipped with a 10.6-eV lamp was used to generate real-time measurements of volatile organic compounds (VOC) in the soil atmosphere. A calibration curve was generated before each use with known concentrations of isobutylene at 0, 0.12, 0.24, 0.48, and 1.2 mg L^{-1}. The PID is a nonspecific total vapor detector and cannot distinguish between detectable compounds in a mixture of gasses (USEPA, 1994). Due to difficulties in ascertaining the exact composition of the fumigant mixtures 2 and 5 d after application, VOC readings were expressed in μL L^{-1} (as isobutylene) rather than as mg L^{-1} of the individual fumigants. Concentrations of VOC were measured in the center of the planting bed at 12 cm depth. Each bed was sampled three times to obtain an average VOC measurement. Additional samples were collected randomly from five separate planting beds. Samples were collected 2 and 5 d after application between 0900 and 1100 h. In the Florida trials, VOC sampling in fumigated beds was extended to 13 d after application. In the Georgia trials, VOC sampling was conducted in the fumigated beds and in the untreated row middles.

Measurement of Vapor and Nonvapor Fumigant Concentrations in the Soil

Soil atmosphere samples were collected using a personal monitoring pump (Model 222; SKC, Eighty-Four, PA) equipped with a XAD4 sorbent tube (Model 226-175; SKC) protected by an anhydrous sodium sulfate drying tube (Model 226-44; SKC). Both tubes were freshly opened at the time of sampling and attached to the pump using 2 to 3 cm of rubber tubing. The pump factor was determined the day before sample collection by setting the pump flow rate to 100 mL min^{-1} using an attached XAD4 sorbent tube and sodium sulfate tandem to approximate sample conditions in the field. At a flow rate of

100 mL min^{-1}, the number of pump counts per minute was determined and used to calculate the pump factor as follows:

Pump factor (mL count^{-1}) = 100/number of counts per 100 mL

Samples were collected at 12 cm depth from the center of the planting beds adjacent to the VOC samples at 2 and 5 d after application. Samples were collected between 0900 and 1100 h using a sample volume of 500 mL. After collection, the sorbent tubes were sealed with plastic caps and immediately transferred to a cooler chilled by dry ice for transfer to the laboratory. Once there, they were stored at $-20°$C until analysis.

For analysis, each section of the XAD4 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 XAD4 tube was added to the 4-mL vial. A combination of 9.8 mL of a 1,2-dichlorobenzene (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 in EtOAc solution was added to the sorbent in the 15-mL vial, and 2.94 mL, 30 μL, and 30 μL of the same solutions were added to the sorbent in the 4-mL vials. In each case, the 1-bromo-4-fluorobenzene served as a surrogate standard, MiI-d3 served as the internal standard for compounds eluting before the solvent, and 1,2-dichlorobenzene served as the internal standard for compounds eluting after the solvent. The vials were capped and allowed to desorb for a minimum of 2 h before analysis. Once desorption was complete, 1 mL of each solution was transferred to a 2-mL crimp-top autosampler vial for analysis. 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 was 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.

Soil samples were collected by transferring approximately 5 g of soil into 40-mL, precleaned, tared, 40-mL volatile organic analysis vials using a "T-bar" 5-g sampling device (Environmental Express, Mount Pleasant, SC). Samples were collected at 2, 5, and 10 cm depths from the center of the planting beds in close proximity to the VOC samples 2 and 5 d after application by punching a hole through the plastic and immediately transferring the soil to vials. Ethyl acetate (10 mL) containing dichlorobenzene (14 mg L^{-1}) was immediately added to the vial using an Eppendorf maxipipette. Vials were sealed, placed in a cooler with dry ice, and transported to the laboratory. Once there, they were stored at $-20°$C until analysis. Samples were collected randomly from five separate planting beds. Before analysis, vials were reweighed, and the masses of the solvent and tare were subtracted to yield the accurate mass of the soil sample.

Analytical standards for 1,3-D, MITC, DMDS, and CP were purchased from Sigma-Aldrich. EtOAc (OmniSolv grade) was purchased from EMD Chemicals (Gibbstown, NJ). XAD4 and sodium sulfate sorbent tubes were purchased from SKC.

The analytical method was developed using a ThermoElectron Polaris Q mass spectrometer equipped with a ThermoElectron trace GC and the AS3000 autosampler and expanded to include use of the ThermoElectron DSQII quadrupole mass spectrometer. Both systems used a 25 m × 0.25 mm × 0.25 μm film DB5 FSOT column with ultra-high purity helium carrier gas with an electronically controlled volume flow of 1.0 mL min^{-1} with vacuum compensation. 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, increased to 50°C at 4°C per minute, and then increased to 120°C and held there for 1 min. The mass spectrometer collection program had three segments. The first segment started at 0.1 min and scanned from m/z 35 to 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 to 200 until the end of the run. The three systems were controlled by Xcalibur 1.4 software (Thermo Fisher Scientific, Inc. Waltham, MA). Compound identification was accomplished by comparing the retention times and full-scan mass spectra with those measured in the calibration standards. Quantitation of the analytes was accomplished by comparing the peak area of extracted ion current profiles in the samples with those in the calibration standards. Method calibration, demonstration of proficiency, and quality control procedures were based on SW846 Chapters 1 and 4 and USEPA Method 8000.

Fumigant Degradation in Soil

Degradation in soil was determined for 1,3-D and CP from soil collected from the Florida trials and for DMDS and MITC from soil collected from the Georgia trials. A composite sample was collected from each site by bulking together seven 2.5 cm × 15 cm cores collected on a transect bisecting the treated area. Samples were placed into double-sealed polyethylene bags and held at 10°C before analysis. Before analysis, soil was passed through a 2-mm sieve, and the water content was determined. Degradation in soil was determined at 25 and 40°C. To differentiate between chemical and microbial fumigant degradation at the different temperatures, natural soil (i.e., the soil as received) and sterilized soil (autoclaved twice for 30 min) were used to determine fumigant degradation. Fumigant degradation in sterile soil was assumed to be chemical degradation, and that in nonsterile soil was assumed to be total degradation. The difference in rate constant between nonsterile and sterile treatments was assumed to be due to microbial degradation. Moist soil (10 g) was placed into 21-mL headspace vials, and 5 μL of acetone containing 40 μg μL^{-1} of the fumigant was added to each vial. Vials were immediately sealed and placed in a constant temperature room at 25 and 40°C. At predetermined times, three replicated samples from each treatment were removed from the incubator and kept in a freezer until fumigant concentration analysis.

Extraction with EtOAc involved shaking moist soil (equivalent to 10 g dry soil) with 10 g anhydrous sodium sulfate and 10 mL EtOAc on a mechanical shaker (200 min^{-1}) for 60 min. An aliquot of the supernatant was transferred into a gas chromatography vial. Analysis of the extracts was performed using an Agilent Technologies 7890C GC equipped with a microelectron capture detector. The column was a DB-VRX 122-1534 with dimensions of 30 m × 250 μM × 1.4 μm (Agilent

Technologies) running at a flow rate of 1.6 mL min⁻¹ and with He as the carrier gas. The inlet temperature was 240°C, and the detector temperature 290°C. The GC oven temperature was maintained at 45°C for 1 min after sample injection, increasing to 75°C at a rate of 2.5°C min⁻¹, and then to 140°C at a rate of 35°C min⁻¹ before being held at this temperature for 3 min. Under these conditions, retention times of *cis* 1,3-D, *trans* 1,3-D, and CP were 10.4, 11.7, and 13.1 min, respectively. A set of 10 standards encompassing the range of *cis* and *trans* 1,3-D and CP concentrations of the samples was prepared in EtOAc. The degradation coefficient was obtained by determining the slope of the natural logarithm of time versus concentration using linear regression for each temperature.

Statistical Methods

To determine the resistance to diffusion (*R*) for plastic films, means were computed from three replicate cells and expressed along with their standard deviation. For fumigant degradation in soil, first-order degradation rate constants (*k*, d⁻¹) of fumigants in field and autoclaved soil were obtained by determining the slope of the natural logarithm of concentration vs. time using linear regression for each temperature. Concentrations of VOCs and individual fumigants in the vapor and nonvapor phase were expressed as the mean and standard error from the five samples collected at each combination of site and time.

Results

Plastic Permeability

Results from the static sealed cell permeability tests are shown in Table 2. The most effective barrier to fumigant diffusion was displayed by VIF. By contrast, LDPE was marginally effective at retarding fumigant diffusion. The metalized film was intermediate between VIF and LDPE as a barrier to fumigant diffusion. Although VIF was the least permeable to fumigants, its resistance to diffusion varied considerably among the fumigants tested. For example, *R* values for the VIF field sample from Florida Site 2 were 2477 and 2.1 for CP and MITC, respectively. In general, VIF provided the most effective barrier to CP, followed by 1,3-D, DMDS, and MITC. Permeability measurements taken after manipulation of the films during

field installation indicated that the permeability of metalized film to CP and 1,3-D increased as a result of stretching the film during installation. The same was true for the combination of DMDS and VIF.

Soil Properties and Environmental Conditions

Soil texture was comprised mostly of fine sand for the Florida trials and was consistent across all three sites (Table 3). The Georgia sites had noticeably higher compositions of silt and clay, with differences observed among the sites. Site 3 had very little clay (0.8%) when compared with Sites 1 and 2 (8.4 and 10.4% clay, respectively). Soil organic carbon at the Florida trials varied from 9.73 to 16.0 Mg ha⁻¹ but was always higher than the Georgia sites, where it ranged from 6.41 to 6.85 Mg ha⁻¹. A large discrepancy in soil characteristics between sites was observed for the relationship between water content of soil at the time of fumigation and water content of those soils at field capacity (−0.033 MPa). Soil moisture at the Florida sites was >200% of field capacity at the time of fumigation (Table 3). High soil moisture content is necessary in the Florida sites to hold the single grain structure of fine sands together to form a raised bed. By contrast, soil moisture at the Georgia sites was below field capacity at fumigant application. Another noticeable difference was the consistency of soil tilth among sites. In the Florida sites, soil in the planting beds had uniform compaction with no noticeable clods. In the Georgia sites, large (>3.00 mm), dense clods of soil were present, particularly in Site 2. The clods prevented uniform compaction of soil under the beds, with noticeable bumps in the covering plastic on the tops and sides of the beds. Ambient air temperatures during fumigant application were similar for the Florida and Georgia sites and are typical for applications made at that time of year (Table 4). Soil temperatures were lower for the Georgia applications. Strong wind speeds were not a factor during fumigant applications, with average wind speeds not exceeding 2.7 m s⁻¹ (Chellemi et al., 2010).

Soil Fumigant Concentrations at the Florida Sites

Volatile organic compound concentrations 2 d after application ranged from 347 at Site 3 to 425 μL L⁻¹ at Site 1 (Fig.

Table 2. Permeability of plastic films to fumigants used in the study.

Trial†	Film type‡	Location	Permeability§				
			cis 1,3-D	trans 1,3-D	CP	MITC	DMDS
			—————————————— h cm⁻¹ ——————————————				
FL sites 1 and 3	metalized	roll	10.6 ± 3.0¶	6.0 ± 2.0	37.0 ± 12.0	NS#	1.8 ± 0.50
FL sites 1 and 3	metalized	field	1.6 ± 0.4	1.0 ± 0.3	5.0 ± 1.0	0.9 ± 0.1	2.7 ± 0.68
FL site 2	VIF	roll	104 ± 3.0	41.0 ± 1.0	3618 ± 292	2.6 ± 0.4	159 ± 24.7
FL site 2	VIF	field	78.0 ± 2.0	28.0 ± 3.0	2477 ± 228	2.1 ± 0.2	80.6 ± 39.5
GA sites 2 and 3	LDPE	roll	0.13 ± 0.01	0.08 ± 0.01	0.37 ± 0.01	0.05 ± 0.01	0.13 ± 0.01
GA sites 2 and 3	LDPE	field	0.13 ± 0.01	0.08 ± 0.01	0.38 ± 0.01	0.05 ± 0.01	0.10 ± 0.01
GA site 1	VIF	roll	601 ± 19	227 ± 4.0	42,466 ± 6230	6.0 ± 3.0	7327 ± 3659
GA site 1	VIF	field	310 ± 94.0	133 ± 28.0	14,672 ± 7468	6.9 ± 0.6	74.8 ± 12.0

† FL, Florida; GA, Georgia.

‡ LDPE, low-density polyethylene; VIF, virtually impermeable film.

§ Permeability (*R*) = 1 *h*⁻¹, where *h* = mass diffusion coefficient.

¶ Values are the mean of three replicate cells ± SD. All films tested at 25°C.

Not sampled.

1). Five days after application, VOC concentrations spiked as high as 600 μL L^{-1} in Sites 1 and 2 but decreased to 244 μL L^{-1} at Site 3. At 13 d after application, VOC concentrations had declined for all sites but still maintained levels ranging from 159 to 188 μL L^{-1} at Sites 1 and 3, respectively.

Concentrations of CP in the soil atmosphere 2 d after application were highest for Site 1, followed by Sites 2 and 3 (Fig. 2). At Day 5, the highest CP concentration was recorded for Site 2. At Site 3, CP concentration was always very low (0.13 μg cm^{-3} of air). Concentrations of 1,3-D and MITC in the soil atmosphere increased from Day 2 to Day 5 (Fig. 2). At Day 2, fumigant concentrations in the nonvapor phase were highest for MITC, followed by 1,3-D and CP (Fig. 3). Nonvapor concentrations of 1,3-D were similar for Sites 1 and 2. Nonvapor concentrations of MITC were larger in Site 1 when compared with Sites 2 and 3. At Day 5, 1,3-D and MITC concentrations in the nonvapor phase were higher in Site 2, the site covered by VIF, when compared with Sites 1 and 2, which were covered by metalized film. Nonvapor concentration of CP was noticeable lower in Site 3 when compared with Sites 1 and 2.

Soil Fumigant Concentrations at the Georgia Sites

Two days after application, VOC concentrations in the soil atmosphere exceeded the detection limits of the photoionization detector (10,000 μL L^{-1}) at all application sites. Five days after application, VOC concentrations continued to exceed the detection threshold at Site 1 (Fig. 4). For Sites 2 and 3, VOC concentrations were 1528 and 1791 μL L^{-1}, respectively. Additional samples collected in the row middles at Day 2 revealed VOC concentrations of 141, 583, and 239 μL L^{-1} for Sites 1, 2, and 3, respectively. Volatile organic compounds detected in the row middles declined to <50 μL L^{-1} by Day 5.

In the soil atmosphere, CP, DMDS, and MITC concentrations at Day 2 were significantly higher at Site 1, which was covered by VIF, when compared with vapor concentrations in Sites 2 and 3, which were covered by LDPE (Fig. 5). Fumigant concentrations in the soil atmosphere declined by Day 5 and were barely detectable for CP and MITC at Sites 2 and 3. Fumigant concentrations in the nonvapor phase were highest at Site 1 on Day 2 (Fig. 6). At Day 5, the highest concentration of fumigants in the nonvapor phase was detected for Site 1 (Fig. 6). No CP was detected in the nonvapor phase at Sites 2 and 3. No MITC was detected for Site 3 at 5 d after application.

Degradation of Fumigants in Soil

The rate of fumigant degradation in soil was adequately described by linear regression of the natural logarithm of time versus concentration for most soil–temperature combinations, as evident by regression coefficients (r^2) > 0.80 (Table 5). The exception was for 1,3-D degradation at several Florida sites, where r^2 values ranged from 0.69 to 0.71, and DMDS in the Georgia sites, where r^2 values ranged from 0.44 to 0.75. A linear model did not appear to adequately describe degradation of DMDS in autoclaved soil, where r^2 values where all <0.80. In field soil, fumigant degradation was more rapid at 40°C when compared with degradation at 25°C, except for DMDS, in which degradation was slower at the higher temperature. At 25°C, the degradation rates of CP, MITC, and DMDS were slower in autoclaved soil. However, degradation of 1,3-D was not affected by autoclaving soil, indicating that very little biological degradation of 1,3-D occurred at 25°C. At 40°C, 1,3-D degradation was reduced in the autoclaved soil, except for the trans isomer at Florida Site 1. In the Florida Sites, degradation was most rapid for CP, followed by 1,3-D and MITC. Degradation rates of CP were noticeably higher in soil from Site 2. At the Georgia sites, degradation was most rapid for DMDS, followed by CP and MITC. Degradation rates for DMDS in the Georgia field soil were similar for Sites 1 and 2 but lower for Site 3.

Discussion

In the Florida trials, monitoring VOC concentrations in the soil atmosphere with the portable PID was extended to 9 and 13 d after application due to high VOC concentrations observed at Day 5. The effectiveness of

Table 3. Characterization of soil properties at the fumigant application sites.

Parameter	Site 1	Site 2	Site 3
Florida trials			
Organic carbon, Mg ha^{-1}	9.73	16.0	13.3
Bulk density, g cm^{-3}	1.49	1.44	1.40
Sand, g kg^{-1}	940	935	960
Silt, g kg^{-1}	35.0	40.0	20.0
Clay, g kg^{-1}	25.0	25.0	20.0
Water content, g kg^{-1}	125	153	144
Water content at 33 kPa suction, g kg^{-1}	51.1	74.0	62.9
% of field capacity (33 kPa suction)	245	206	229
Georgia trials			
Organic carbon content, Mg ha^{-1}	6.85	6.41	6.85
Bulk density, g cm^{-3}	1.50	1.38	1.52
Sand, g kg^{-1}	792	812	860
Silt, g kg^{-1}	124	84	132
Clay, g kg^{-1}	84.0	104	8.00
Water content, g kg^{-1}	83.0	99.0	81.0
Water content at 33 kPa suction, g kg^{-1}	117	152	109
Moisture relative to field capacity, %	71	65	74

Table 4. Environmental conditions at time of application.

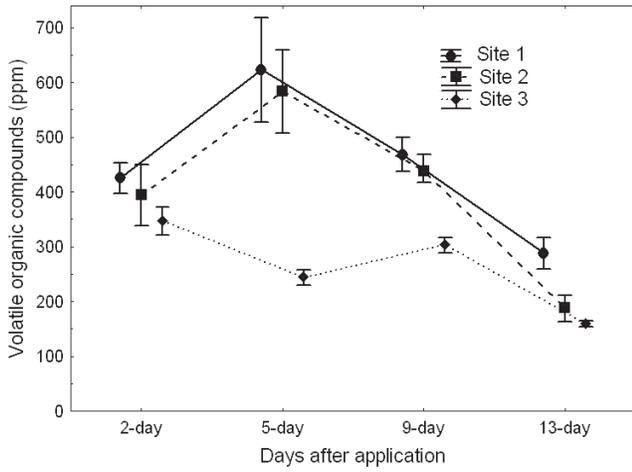|	Site 1	Site 2	Site 3
Duette, FL			
Ambient temperature, °C	18.0	19.4	19.4
Soil temperature at 15 cm depth, °C	15.8	18.0	19.2
Wind speed, m s^{-1}	0.90	0.70	0.40
Tifton, GA			
Ambient temperature, °C	21.1	20.0	15.6
Soil temperature at 15 cm depth, °C	9.20	11.1	13.3
Wind speed, m s^{-1}	2.70	2.20	0.20

Fig. 1. Concentration of volatile organic compounds at the Florida sites at 2, 5, and 13 d after application. Air samples were collected at a 12-cm depth in the center of the bed. 1,3-Dichloropropene was not applied to Site 3. Sites 1 and 3 were covered by metalized film; Site 2 was covered by virtually impermeable film.
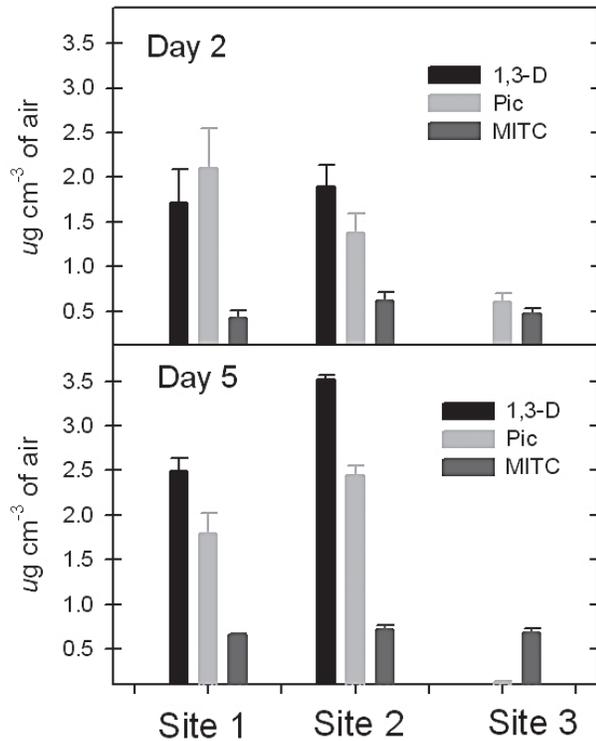

Fig. 2. Concentration of soil fumigants in the soil atmosphere at the Florida sites at 2 and 5 d after application. Air samples were collected at a 12-cm depth in the center of the bed. 1,3-Dichloropropene (1,3-D) was not applied to Site 3. Sites 1 and 3 were covered by metalized film; Site 2 was covered by virtually impermeable film. MITC, methyl isothiocyanate; Pic, chloropicrin.

chemical fumigants in the soil is determined by its time weighted exposure concentration (i.e., CT value) (Munnecke and van Gundy, 1979). Thus, for the Florida trials, it is reasonable to assume that an improvement in fumigant efficacy may be realized through its prolonged retention in soil, particularly in the vapor phase, and may offer possibilities for additional reductions in application rates. Prolonged soil retention also reduces atmospheric emissions, a critical health and environmental concern regarding soil fumigants. Drawbacks to
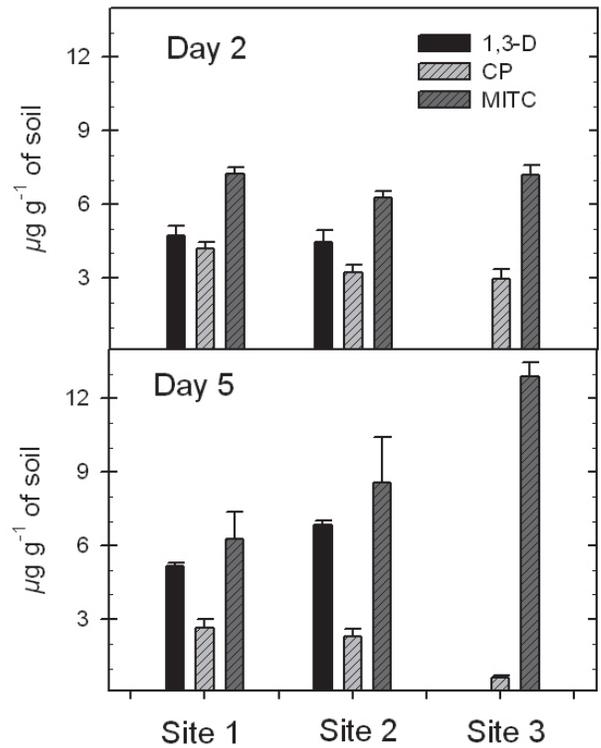

Fig. 3. Nonvapor phase concentration of soil fumigants at the Florida sites at 2 and 5 d after application. 1,3-Dichloropropene (1,3-D) was not applied to Site 3. Sites 1 and 3 were covered by metalized film; Site 2 was covered by virtually impermeable film. CP, chloropicrin; MITC, methyl isothiocyanate.
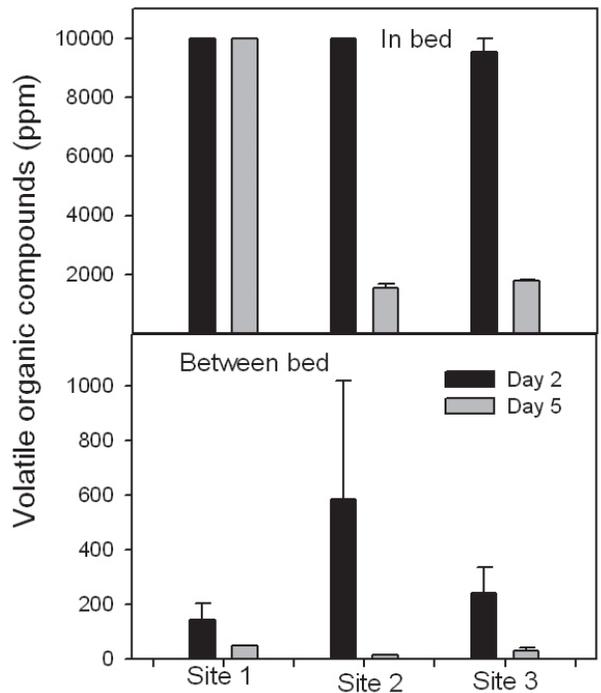

Fig. 4. Concentration of volatile organic compounds at the Georgia sites at 2 and 5 d after application. Air samples were collected at a 12-cm depth in the center of the bed. Site 1 was covered by virtually impermeable film; Sites 2 and 3 were covered by low-density polyethylene.

increased fumigant retention in soil are the possibility for movement into surface or ground water, particularly if the fumigant
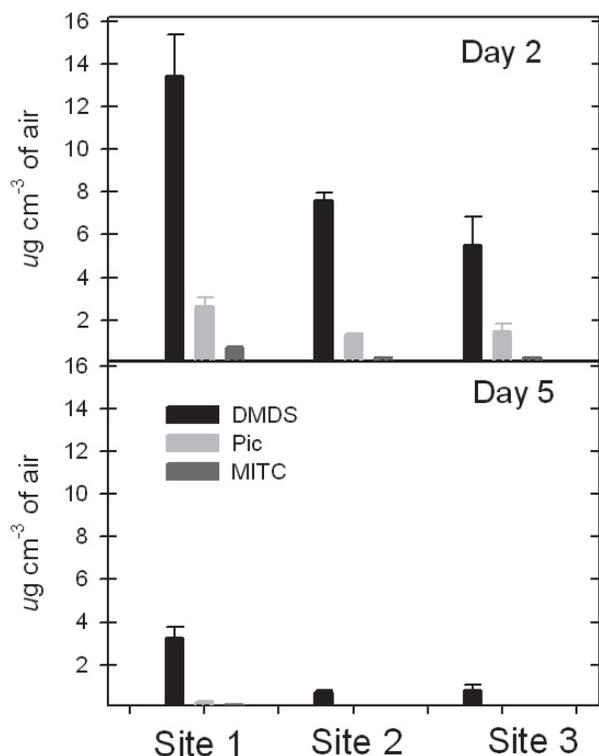
Fig. 5. Concentration of fumigants in the soil atmosphere at the Georgia sites at 2 and 5 d after application. Air samples were collected at a 12-cm depth in the center of the bed. Site 1 was covered by virtually impermeable film; Sites 2 and 3 were covered by low-density polyethylene. DMDS, dimethyl disulfide; MITC, methyl isothiocyanate; Pic, chloropicrin.
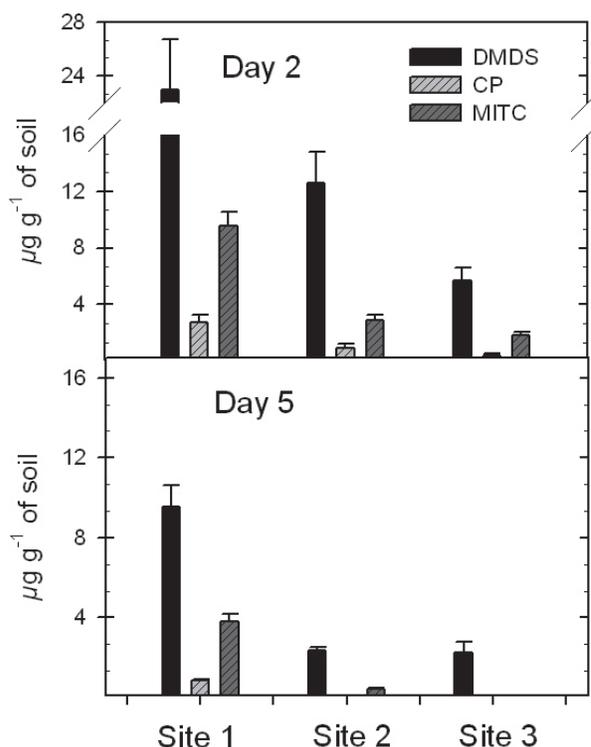

Fig. 6. Nonvapor phase concentrations of soil fumigants concentrations at the Georgia sites at 2 and 5 d after application. Site 1 was covered by virtually impermeable film; Sites 2 and 3 were covered by low-density polyethylene. DMDS, dimethyl disulfide; MITC, methyl isothiocyanate; Pic, chloropicrin.

is in the nonvapor phase, and the potential of increased plant back times due to the threat of phytotoxicity to crops.

In the Georgia trials, olfactory detection of fumigant vapors on Day 2 by workers in the field indicated a higher level of atmospheric emissions. Access to a portable PID in the field during samplings permitted immediate on-site collection of additional air samples from the untreated row middles. Detection of high VOC concentrations in the row middle identified an additional source for elevated atmospheric unrelated to the use of plastic film barriers. It is suspected that extended pore spaces under the plastic, created by the presence of large soil clods and undecomposed plant residue in the beds, provided a channel for the fumigants to escape into the untreated row middles.

The rate of fumigant degradation in soil varied depending on the fumigant tested, soil temperature, and specific application site. Degradation of CP was attributed primarily to microbial activity based on the difference in degradation rates between sterile and nonsterile soil. In this study, it is estimated that microbial degradation accounted for 55 to 91% of the overall CP degradation at 25°C. Similar results were obtained by Gan et al. (2000), who estimated that microbes accounted for 68 to 92% of the overall CP degradation. At 40°C, the relative contribution of microbes to fumigant degradation was diminished in five of the six application sites, ranging from 17 to 74%. In soils, CP is dehalogenated by *Pseudomonas* spp., most notably *Pseudomonas putida* (Castro et al., 1983; Wilhelm et al., 1996). Survival of *P. putida* in soil temperatures of 40°C is uncommon (Srivastava et al., 2008). Thus, observed reductions in micro-

bial degradation at 40°C are attributed to thermal inactivation of heat-sensitive *Pseudomonas* spp. For DMDS, the contribution of soil microbes to fumigant degradation at 25°C was 95 to 96% of the overall DMDS degradation and appears to be even larger than their observed contribution to CP degradation. Similar to the trend observed with CP, the contribution of soil microbes to degradation of DMDS at 40°C was reduced to 45 to 69% of the overall degradation, indicating the thermal sensitivity of DMDS degrading microbial communities. Microbial groups contributing to DMDS degradation in soil include thiosulfate- and sulfur-reducing bacteria, which have optimum temperatures for growth below 40°C (Escoffier et al., 2001). For 1,3-D, similar degradation rates in field and autoclaved soil were observed, indicating that abiotic factors were largely responsible. In Georgia, the relative contribution of biotic and abiotic factors to MITC degradation varied between the sites. For Site 3, MITC degradation was primarily attributed to abiotic factors at both temperatures studied (Table 5). For soil from Site 2, MITC degradation was largely due to biological factors. For Site 1, biotic degradation occurred primarily at 25°C, whereas abiotic factors were largely responsible for MITC degradation at 40°C. Microbial degradation of 1,3-D, CP, and MITC has been reported in soils from other regions (Dungan and Yates, 2003; Gan et al., 1999; Gan et al., 2000). It is suspected that further variability will occur when multiple fumigants are applied due to the nontarget effects of the coapplied fumigant on microbial communities. Zheng et al. (2003) observed competitive degradation with 1,3-D accelerating the degradation of CP. In the Florida trials, vapor concentrations

of CP were higher in Site 3, which did not receive a coapplication of 1,3-D (Fig. 2), whereas nonvapor concentrations of CP were similar among the two sites, indicating that competitive degradation did not occur in this study.

In this study, observed disparities in the persistence of MITC and CP in soil after application are attributed to the combined effect of soil moisture, soil tilth, and plastic film. Soil temperatures monitored over the 5-d fumigation period were higher in the Florida sites when compared with the Georgia sites (Chellemi et al., 2010). However, CP and MITC concentrations in soil were noticeably greater in the Florida sites 5 d after application (Fig. 3 and 6). Furthermore, fumigant applications were made in January and February, the coolest months of the year. Thus, it is postulated that in this study, soil temperatures did not play a critical role in the observed differences in fumigant persistence between the application sites. Soil moisture played a very large role in the soil fate of fumigants after application and can be used to partially explain the discrepancies observed between the Florida and Georgia applications. In the Florida applications, soil water content was >200% greater than the water content at field capacity, whereas in Georgia, water content was well below field capacity during application. Field capacity is defined as the content of water remaining in soil after gravitational water and readily displaced water at high matric potentials (greater than −0.03 MPa) have drained (i.e., soil macropores are empty) (Hartel, 1998). Assuming simple Henry's Law partitioning, this would imply that much more fumigant would be present in the water phase at the Florida sites compared with the Georgia sites. Regarding to the movement of the fumigants in soil after application, the optimum soil moisture for most soil fumigations ranged from −0.06 to −1.5 MPa, well below field capacity (Munnecke and van Gundy, 1979). Drier soils also promote higher emissions because vapor diffusion dominates movement. Although raised planting beds are ideal for movement of fumigant vapor through soil, it is very difficult to prepare them with uniform compaction in sandy soil when soil moisture is below field capacity (D.O. Chellemi, personal observations). Soil texture at the Florida sites was predominantly sand (93.5–96.0%), whereas soil texture at the Georgia sites had lower sand content (79.2–86.0%). Thus, for raised-bed plastic mulched production systems, it is expected that fumigant retention in sandy textured soil will be increased due to higher water content during bed preparation. Higher water content reduces subsurface dispersion of 1,3-D and CP and increases their residence time in soil (Cryer and Wesenbeck, 2009; Gan et al.,

Table 5. First-order degradation rate constants of fumigants in field and autoclaved soil at 25°C and 40°C.

Site	Field soil, 25°C	Autoclaved soil, 25°C	Field soil, 40°C	Autoclaved soil, 40°C
		————————————————— d^{-1} —————————————————		
		Florida trials		
Chloropicrin				
1	1.71 (0.93)	0.24 (0.93)†	3.83 (0.98)	0.98 (0.96)
2	4.91 (0.97)	0.42 (0.96)	17.3 (0.97)	1.92 (0.99)
3	1.21 (0.93)	0.26 (0.87)	1.47 (0.96)	0.91 (0.96)
1,3-dichloropropene (cis)				
1	0.13 (0.70)	0.13 (0.91)	0.57 (0.98)	0.45 (0.99)
2	0.17 (0.81)	0.16 (0.94)	0.72 (0.99)	0.47 (0.99)
3	0.17 (0.94)	0.14 (0.71)	0.73 (0.98)	0.45 (0.98)
1,3-dichloropropene (trans)				
1	0.11 (0.92)	0.14 (0.69)	0.55 (0.97)	0.58 (0.99)
2	0.14 (0.93)	0.16 (0.84)	0.72 (0.99)	0.52 (0.97)
3	0.14 (0.71)	0.17 (0.92)	0.84 (0.99)	0.42 (0.91)
Methyl isothiocyanate				
1	0.08 (0.98)	0.05 (0.90)	0.27 (0.99)	0.15 (0.99)
2	0.10 (0.98)	0.04 (0.87)	0.31 (0.99)	0.22 (0.99)
3	0.10 (0.98)	0.05 (0.94)	0.32 (0.99)	0.18 (0.98)
		Georgia trials		
Chloropicrin				
1	0.40 (0.95)	0.18 (0.95)	0.58 (0.88)	0.33 (0.94)
2	0.37 (0.94)	0.13 (0.93)	0.52 (0.85)	0.43 (0.97)
3	0.36 (0.87)	0.15 (0.96)	0.58 (0.92)	0.40 (0.98)
Methyl isothiocyanate				
1	0.12 (0.98)	0.05 (0.93)	0.43 (0.98)	0.77 (0.96)
2	0.28 (0.99)	0.08 (0.95)	0.96 (0.99)	0.27 (0.93)
3	0.07 (0.95)	0.05 (0.92)	0.30 (0.98)	0.21 (0.77)
Dimethyl disulfide				
1	0.60 (0.92)	0.03 (0.44)	0.26 (0.81)	0.08 (0.75)
2	0.68 (0.93)	0.03 (0.44)	0.28 (0.90)	0.09 (0.71)
3	0.44 (0.74)	0.02 (0.43)	0.11 (0.68)	0.06 (0.50)

† Numbers in parentheses are regression coefficients.

1998; Gao et al., 2008; Thomas et al., 2004). Soil moisture was shown to have a greater impact on vapor and nonvapor concentrations of CP than 1,3-D in soil columns adjusted at several moisture levels below field capacity (Qin et al., 2009).

Tilth is defined as the physical condition of soil as related to its ease of tillage, fitness as a seedbed, and its promotion of seedling emergence and root penetration (Karlen, 2005). Soils with poor tilth are described as being cloddy (Karlen, 2005). There was a very noticeable difference in the size, frequency, and density of soil clods present at the Florida and Georgia sites. For the Florida sites, frequent cultivation to facilitate the breakdown of nondecomposed crop residue was used before fumigation. Together with higher organic carbon content, soil moisture, and cation exchange capacities (data not presented), this led to improved tilth at the Florida site, allowing uniform soil compaction in the fumigated beds. By contrast, the Georgia sites contained partially decomposed crop residues, which, combined with lower soil moisture, lower cation exchange capacities, lower soil organic matter, and higher silt and clay contents, resulted in the presence of numerous large clods of soil. Cloddy soil results in large air pockets that facilitate fumigant volatilization and diffusion through the soil profile. This was responsible for the detection of VOCs in between beds at the Georgia sites. Tilth is difficult, if not impossible, to quantify and is often easier for a farmer to recognize than for a scientist to describe (Karlen, 2005).

For the Florida sites, retention of fumigants in soil through the combined contributions of high soil moisture (>200% above field capacity) and improved tilth were significant enough to override the differences in the permeability of plastics to fumigants. For example, evidence showed similar soil vapor and nonvapor concentrations of 1,3-D, MITC, and CP between sites with metalized film or VIF. Furthermore, when comparing the fate of CP and MITC in soil under VIF, fumigant persistence was dramatically greater in the site with high soil moisture and better field preparation (Florida Site 2) than the site with cooler soil temperatures and heavier (more clay and silt) soils (Georgia Site 1). Detection of VOCs in the untreated row middles at the Georgia VIF site (Fig. 5) demonstrates how low moisture and poor field preparation reduced the benefits of VIF. The contribution of field preparation, including formation of the raised, plastic-mulched beds, cannot adequately be simulated in laboratory or microplot studies. Thus, this study is unique in its elucidation of those combined effects on the fate of fumigants in soil.

Plastic permeability had a major impact on fumigant persistence in soil in this study when the fumigant applications were made under less than ideal soil conditions, as evidenced at the Georgia sites. There, fumigant concentrations in the vapor and nonvapor phases were greatest under VIF (Site 1) when measured 2 and 5 d after application (Fig. 5 and 6). Furthermore, analysis of fumigant flux from soil in a study associated with the Florida and Georgia trials demonstrated reduced flux and cumulative atmospheric emissions under VIF in the Georgia sites (Chellemi et al., 2010). Thus, to minimize atmospheric emissions and to ensure efficacy when application conditions are less than ideal, VIF should be used during the application process. Extending fumigant retention in soil through the use of VIF can increase the potential for high concentrations of

fumigant vapors to remain during planting or tarp cutting, escalating the risk of crop injury or worker exposure. To mitigate the unintended consequences of excessive fumigant retention in soil, application rates associated with VIF should be adjusted to allow for their degradation in soil through naturally occurring biotic and abiotic mechanisms.

Summary

The soil fate of agricultural fumigants after their application was determined in field trials conducted in Florida and Georgia. At 5 d after application, MITC and CP were detected in the nonvapor phase at concentrations up to 11.61 and 2.78 $\mu g\ g^{-1}$ of soil, respectively, in the Florida trials and 4.38 and 0.82 $\mu g\ g^{-1}$ of soil, respectively, in the Georgia trials. Ranked in the order of the magnitude of their contribution, factors that affected fumigant persistence in soil were soil moisture, field preparation, plastic film, and soil type. Soil moisture exceeding field capacity, uniform soil tilth with an absence of large clods and undecomposed plant residue, and VIF and metalized films were specific GAPs that improved retention of fumigants in soil. In the Florida trials, VOC concentrations in the soil atmosphere 13 d after application indicated the extended persistence of fumigants, which can improve their efficacy but also extend the plant back intervals and increase the potential for off-site movement of the chemical fumigants. Rapid loss of fumigants from bedded soil profiles covered by LDPE indicated the potential for increased atmospheric emission, particularly when soil moisture and tilth are not optimum. In an associated study of atmospheric emissions from the same fumigant applications, increased emissions under LDPE were realized (Chellemi et al., 2010).

Acknowledgments

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