Atmospheric emissions of methyl isothiocyanate and chloropicrin following soil fumigation and surface containment treatment in bare-root forest nurseries

D. Wang, J. Juzwik, S.W. Fraedrich, K. Spokas, Y. Zhang, and W.C. Koskinen

Abstract: Methylisothiocyanate (MITC) and chloropicrin (CP) are alternatives to methyl bromide for soil fumigation. However, surface transport of MITC emission has been cited as the cause for seedling damage in adjacent fields at several bare-root forest-tree nurseries. Field experiments were conducted at nurseries in Wisconsin and Georgia to measure air emissions of MITC and CP after fumigation. Four treatments were tested as combinations of two fumigants (dazomet or coapplication of CP and metam sodium) and two surface containment treatments (tarp or water seal). A very small percentage (<5%) of the applied equivalent of MITC was lost through either surface treatment over a 2-week period, and lower emissions occurred with the water seal. Cumulative emissions of CP accounted for 10%–22% of the applied CP. With all surface containment treatments, more than 70% of total cumulative emissions of either MITC or CP occurred within 1 week of application. Either surface containment treatment can be used by nursery managers to reduce risk of MITC emissions that could cause damage to nearby seedling crops or harm to humans.

Résumé : L'isothiocyanate de méthyle (ITCM) et la chloropicrine (CP) peuvent remplacer le bromure de méthyle pour la fumigation du sol. Cependant, des dommages aux semis dans les champs adjacents ont été imputés au transport en surface des émissions d'ITCM dans plusieurs pépinières forestières à racines nues. Des expériences de terrain ont été réalisées dans des pépinières du Wisconsin et de la Géorgie pour mesurer les émissions d'ITCM et de CP après une fumigation. Quatre traitements constitués des combinaisons de deux fumigants (dazomet ou application combinée de CP et de métam-sodium) et deux types de confinement en surface (bâche ou scellant aqueux). Peu importe le type de confinement en surface, un très faible pourcentage (<5 %) d'équivalent d'ITCM appliqué s'est échappé sur une période de deux semaines et les émissions ont été les plus faibles avec le scellant aqueux. Les émissions cumulatives de CP représentaient 10 % à 22 % de la quantité de CP appliquée. Plus de 70 % des émissions cumulatives totales d'ITCM et de CP sont survenues en moins d'une semaine après l'application quel que soit le type de confinement utilisé. N'importe quel type de confinement peut être utilisé par les gestionnaires de pépinière pour réduire les risques d'émission d'ITCM susceptible de causer des dommages aux semis avoisinants ou du tort aux personnes.

[Traduit par la Rédaction]

Introduction

Soil fumigation is commonly used in bare-root forest nurseries to manage soilborne pests including fungal pathogens, nematodes, weeds, and insects. Formulations of methyl bromide and chloropicrin were the most commonly used fumigant treatments in USA forest nurseries in the early 1990s (Smith and Fraedrich 1993). However, bromine resulting from breakdown of methyl bromide contributes to loss of the Earth stratospheric ozone layer (Yagi et al. 1993), and methyl bromide use is regarded as an important cause of ozone depletion. Since the early 1990s there has been considerable investment in research in the USA to find effective, economical, and more environmentally benign alternatives to methyl bromide. Production of methyl bromide for use as a soil fumigant has been scheduled to end in 2005 in accordance with the United States Clean Air Act and the Montreal Protocol (US Environmental Protection Agency 2004*a*), although exemptions are being proposed on a yearly basis in the United States for some crops including forest-tree seedlings (Thompson 2003) because of perceived problems with available alternatives.

Dazomet and metam sodium, methyl isothiocyanate (MITC) generators, and chloropicrin (CP) are possible alternatives for methyl bromide in northern and southern forest nurseries (Cram et al. 2002; Fraedrich and Dwinell 2003; Juzwik and Pokorny 2003; South et al. 1997). Dazomet and metam sodium have been used effectively in a small number of nurseries in

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these regions for many years (Borkenhagen 1994; Chapman 1992; S. Gilly, personal communication, 2005). Fumigation with a combination of CP and metam sodium was found to be as effective as methyl bromide and chloropicrin for reducing weeds in a recent southern nursery study (Carey 2000*a*). In addition, populations of *Macophomina phaseolina* were significantly reduced by soil fumigation with dazomet and metam sodium in a Florida nursery (Barnard et al. 1994).

The effectiveness of dazomet for seedling production and pest control has been variable in forest nurseries (Smith and Fraedrich 1993; Borkenhagen 1994), and reported differences in performance may be due to a combination of factors including soil type, target pests, and application techniques (Landis and Campbell 1991). Dazomet is a granular, broad-spectrum fumigant that is spread on the soil surface, incorporated into the soil, and activated by soil water to produce MITC (US Environmental Protection Agency 2004*b*; Pennington 1995). Effectiveness of the chemical is increased by the use of polyethylene tarps or by surface compaction followed by irrigation to create a water seal. These surface treatments prolong the exposure of soil-borne pests to MITC. Daily irrigation is recommended to maintain the water seal (Pennington 1995), which can also reduce atmospheric emissions of MITC (Wang et al. 1997*a*; Gan et al. 1998). Guidelines for dazomet application in northern nurseries have been refined to include proper selection of incorporation equipment and chemical rate based on depth of the target organisms (Juzwik et al. 2001). In addition, soil pH, organic matter content, and state variables such as moisture and temperature can affect the efficacy of dazomet (Landis and Campbell 1991). Metam sodium is available in a number of commercial products and may be applied in different ways (e.g., shank injected, through irrigation systems, or sprayed on surface and incorporated into soil). CP is shank-injected into soil at 15–20 cm in depth, and the gas disperses within the soil profile. CP is normally contained in soil with tarps, and metam sodium is normally contained with tarps or water seal.

Current information on the distribution of MITC in forest nursery soils is largely qualitative being based on results of radish or lettuce seedling germination assays of soil collected at different depths shortly after fumigation (Kelpas and Campbell 1994; Juzwik et al. 1997). Gas movement through the soil and through surface treatments leads to atmospheric emissions of fumigant gases. Reports of atmospheric emissions from alternative fumigants and subsequent collateral seedling damage have been one of the arguments advanced for seeking critical use exemptions for methyl bromide (Barham 2002; McNabb 2002).

In at least four documented cases, surface transport of such emissions was cited as the cause of significant seedling losses in adjacent fields. Pine seedling losses occurred in Texas and Mississippi nurseries following coapplication of metam sodium and CP without tarps (Carey 2000*b*; Barham 2002; McNabb 2002). Drift of air emissions resulting from fumigation with metam sodium in a Washington nursery (Buzzo 2003) and from fumigation with dazomet in an Oregon nursery (Scholtes 1989) were also associated with damage in adjacent seedling crop fields. Concerns also exist over the buffer distance required to protect inhabitants of dwellings near treated fields following fumigation with chemicals such as metam sodium and CP because of potential off-site movement of gas emissions (California Department of Pesticide Regulations 2004). In at least one of the instances where fumigants had moved off site because of atmospheric emissions, litigation was pursued against the contract fumigator by individuals possibly exposed to the chemical drift (Barham 2002). To our knowledge, no published literature exists on the levels of MITC and CP escaping to the atmosphere through either tarp or surface compaction with water-seal treatment in forest-tree nurseries. Such information would be valuable to nursery managers seeking to reduce negative environmental impacts following soil fumigation. Specifically, managers could adopt methods shown to produce lower levels of emissions to reduce the possibility of injury to adjacent crops as well as reduce health risks to nursery workers and nearby building inhabitants.

Studies were initiated in 2002 to measure subsurface distribution and atmospheric emissions of MITC and CP following fumigation with dazomet or a combination of metam sodium and CP in bare-root forest nurseries in Wisconsin and Georgia. Nurseries with well-drained soil types and histories of fumigation were selected for the study. Nurseries in different regions of the United States were used to provide information on fumigant emission levels under different climatic conditions. Results of the air emissions occurring through two surface containment treatments (tarp and water seal) are presented in this paper. Results of subsurface gas levels in relation to effects on soil-borne fungi and weed propagule viability will be published separately.

Materials and methods

Study sites and experimental design

Two related field trials were conducted at the Hayward State Forest Nursery, Hayward, Wisconsin, USA (46°00′N, 91°30′W) and the Flint River Nursery, Byromville, Georgia, USA (32.2°N, 84.0°W). Selection of study sites was based on soil fumigation history, dissimilarity in latitude, availability of fields for research, and offers of technical assistance. The Hayward soil is a Vilas loamy sand (sandy, mixed, frigid, Entic Haplorthod), and the Georgia soil is a Eustis loamy sand (siliceous, thermic, Psammentic Paleudalt). Additional soils information can be found in Table 1. The study fields have been in forest seedling production for 15 years in Georgia and at least 50 years in Wisconsin. Four fumigation methods were used as combinations of two fumigants (dazomet or a coapplication of metam sodium and CP) and two surface containment treatments (tarp or water seal). The study fields were split into two with water seal tested in one section and tarps in the other. The experimental design within each section was a randomized complete block with four replications. Plots were 2.4 m × 9.1 m, with a buffer (9.1 m) between plots.

Fumigant and surface treatments

Dazomet granules (99% active ingredient, Basamid™ Granular, BASF Corp., Memphis, Tennessee, USA) were applied to the appropriate plots in Wisconsin with a tractor-drawn, drop-type spreader on 7 August 2002 at either a rate of 448 kg·ha^{-1} or 336 kg·ha^{-1}. The chemical in the high rate plots was incorporated to 20 cm in depth with a spading

Table 1. Nursery site location and soil properties.

Nursery site (lat., long.)	Depth (cm)	pH	Bulk density ($g \cdot cm^{-3}$)	Sand (%)	Silt (%)	Clay (%)	TOC (%)*
Hayward, Wisconsin (46°00′N, 91°30′W)	0–10	5.8	1.49	83.7	9.0	7.3	1.1
	10–20	5.8	1.63	86.7	6.5	6.8	1.1
	20–30	5.6	1.72	93.5	1.7	4.8	0.1
	30–50	5.9	1.77	96.2	0.3	3.5	<0.1
	50–75	6.1	1.75	97.8	0.0	2.2	<0.1
Byromville, Georgia (32°09′N, 83°58′W)	0–15	5.6	1.26	86.2	7.3	6.5	1.4
	15–30	5.9	1.46	85.9	6.8	7.3	1.4
	30–45	6.0	1.63	86.2	6.5	7.3	1.4
	45–60	5.0	1.62	83.9	7.8	8.3	1.1

*TOC, total organic carbon.

machine (Gramegna V84/30B), while the chemical in the low rate plots was incorporated to 12 cm in depth with a rotary tiller (Kuhn EL80N). Dazomet granules were applied to plots in Georgia using a hand-operated, drop-type spreader on 9 September 2003 at a rate of 560 $kg \cdot ha^{-1}$. The chemical was incorporated to 20 cm with a rotary tiller (Bush Hog – RTH88). The dazomet rates used were within the manufacturer-recommended range and were the rates typically used at the respective nurseries.

Metam sodium (0.5 kg metam $sodium \cdot L^{-1}$, Vapam™ HL, AMVAC, Los Angeles, California, USA) was sprayed on the soil surface of appropriate plots on 6 August 2002 in Wisconsin and 9 September 2003 in Georgia at a rate of 686 $L \cdot ha^{-1}$. Immediately after application, the chemical was incorporated to 12 cm in depth in Wisconsin and 20 cm in depth in Georgia with a rotary tiller. Within 2 h of metam sodium application and incorporation, chloropicrin (Chlor-O-Pic™, Great Lakes Chemical Corp., West Lafayette, Indiana, USA) was shank-injected (by Hendrix and Dail, Inc., Cairo, Georgia, USA) at 20–25 cm in depth in the same plots at a rate of 168 $kg \cdot ha^{-1}$.

The soil surface of all plots in the water-sealed portion of the study field in each location was compacted with a tractor-pulled roller after dazomet or metam sodium plus chlorpicrin treatment. Irrigation water was applied daily for 7 consecutive days to establish and maintain a water seal. Targeted amounts of irrigation water for these days (2.54 cm on days 1 and 2, 1.69 cm on days 2 and 3, and 1.25 cm for days 4–7) were based on manufacturer recommendation for dazomet (Pennington 1995). High-density polyethylene tarps (1-mil or 0.025 mm, manufactured by Cadillac Plastics, Inc., per Hendrix and Dail, Inc.) were placed over appropriate dazomet or metam sodium plus chloropicrin plots in each location, and the edges were sealed with soil. Tarps remained in place for more than 2 weeks.

Water and temperature monitoring

Rain gauges were installed inside and outside of the water-sealed plots to measure water delivered via irrigation and rain at each location. Readings were made before and after each irrigation or rain event. Soil water content was measured in the tarped and water-sealed plots at multiple depths using an automated time-domain reflectometry system (Wang et al. 1998*a*). Air and soil temperatures were measured in tarped and water-sealed plots (multiple depths for soil) using an automated thermocouple system (Wang et al. 1998*a*). Soil water and temperature measurements were recorded electronically every 5 min, and ranges and averages were determined hourly.

Emissions sample collection

At both sites, atmospheric emissions of MITC and CP were measured with passive flux chambers modified from heavy-duty aluminum trays (25 cm wide × 47 cm long × 16 cm deep). Passive chambers were more desirable because they could be placed on plots only during measurements and would not interfere with the water-seal treatment. For emission measurements from the tarp-covered plots, a collar was sealed on the tarp to provide physical support for the chambers and to protect tarps from puncture during measurements.

Because emission fluxes can be very dynamic, especially during the first few days after fumigation (Majewski et al. 1995; Yates et al. 1996*a*), samples were collected every 3 h during the first 3 days. Incrementally longer sampling intervals were used later, and the emission sampling continued for at least 17 days. To capture volatilized MITC and CP, 60 mL of air was drawn from the chambers through activated charcoal (for MITC) and polymer-based XAD tubes (for CP) (Supelco Inc., Bellefonte, Pennsylvania, USA) at 0, 2, 5, and 10 min after chamber placement during the first 5 days after fumigation. Longer placement times (30 min) and sampling intervals (at 0, 10, 20, and 30 min after placement) were used after 5 days. The emission fluxes were calculated as:

$$[1] \qquad \text{flux} = \frac{V}{A}\left(\frac{\Delta C}{\Delta t}\right)$$

where V is the chamber volume (18.80 L), A is the chamber surface area (0.12 m^2), and C/t is the slope of fumigant concentration versus time. The emissions calculations were based on data that exhibited a linear trend ($r^2 > 0.90$) during the four sampling intervals.

Sample analyses

Analytical procedures for determining the amount of fumigants absorbed on the sample tubes were modified from Gan et al. (1994). Analyses were made using a gas chromatograph (Hewlett-Packard 5890A) with an electron capture detector and a nitrogen–phosphorus detector connected to a headspace autosampler (Hewlett-Packard HP-7694). The autosampler was equipped with a 1-mL sample loop, which was split between two columns each going to a separate detector.

A 30 m × 0.53 mm × 5 μm RTX-5 capillary column (Restek Corp., Bellefonte, Pennsylvania, USA) was used for MITC at a flow rate of 5 mL·min^{-1}, and a 30 m × 0.53 mm × 3 μm RTX-624 capillary column (Restek Corp.) for CP with a flow rate of 5 mL·min^{-1}. For MITC analysis, the entire contents of each charcoal tube were transferred into a 21-mL headspace vial. After adding 2 mL ethyl acetate, the vial was immediately capped with Teflon™-lined butyl rubber septa and crimped with an aluminum seal. The vials were then run on the gas chromatograph, and the amount of MITC present was quantified using the nitrogen–phosphorus detector. The oven was held at 90 °C for 7 min, and the nitrogen–phosphorus detector was held at 220 °C. The response of this detector over the concentration range of MITC (0.01–500 μg) was linear ($r^2 > 0.98$), and the amount of MITC in each tube was calculated by comparing the sample response to the standards. A calibration standard (Chem Service, Bellefonte, Pennsylvania, USA) was added for every 30 samples. The detection limit of MITC was 0.01 μg, which would correspond with 0.17 mg·m^{-3} for a 60-mL sample. Vials were run within 2 days of extraction and held at –20 °C until analyzed. Similar procedures were used for CP, except that 2 mL benzyl alcohol was added to each vial as the solvent and the amount of CP was quantified using the electron capture detector. The oven was held at 70 °C for 7 min, and the electron capture detector was held at 250 °C. The response of this detector over the concentration range of CP (0.01–5000 μg) was also linear ($r^2 > 0.93$) with a detection limit of 0.01 μg.

Results

Water and temperature conditions

Owing to irregularities in water pressure in the irrigation systems in the Wisconsin nursery, the actual amount of irrigation water delivered was 1.3 cm on day 1 (after fumigant application), 2.5 cm on day 2, 2.8 cm on day 3, 4.2 cm on day 4, 3.2 cm on day 5, 1.2 cm on day 6, 1.7 cm on day 7, and 1.3 cm on day 8 (Fig. 1). Irrigations on day 4 (2.0 and 2.2 cm) and day 5 (1.9 and 1.3 cm) were split into morning and afternoon applications. In the Georgia nursery, water-sealed plots received 1.5 cm of water immediately after application of fumigants. Irrigation of 2.3 cm was made on day 2, 1.5 cm on day 3, 0.9 cm on day 4, 0.8 cm on day 5, 0.5 cm on day 6, and 0.8 cm on day 7. Irrigations on day 2 (1.5 and 0.8 cm), day 3 (1.0 and 0.5 cm), and day 4 (0.5 and 0.4 cm) were split into morning and afternoon applications. The sum of irrigation and rainwater by the 8th day after fumigant application was 18.6 cm at Wisconsin and 8.3 cm at Georgia. Beyond the first week, rain occurred on days 11 and 15 after application of fumigants in Wisconsin and on day 14 in Georgia (Figs. 1*a*, 1*b*).

During the first week following treatments, soil moisture contents at 10 cm in depth fluctuated between 0.23 and 0.28 cm^3·cm^{-3} in Wisconsin, and between 0.17 and 0.22 cm^3·cm^{-3} in Georgia (Figs. 1*c*, 1*d*). Soil moisture at 30 cm and lower depths remained low (about 0.15 cm^3·cm^{-3}) in Wisconsin. However, consistently higher soil moisture (0.20 cm^3·cm^{-3}) occurred at 30 cm and lower depths in Georgia, where a compacted soil layer was found at 40 cm (bulk density 1.63 g·cm^{-3}, Table 1). Except for a thin gravel layer at 30 cm, no compacted layer occurred in the Wisconsin field.

Ambient air temperature in Wisconsin fluctuated between 5 and 27 °C with low nighttime temperatures occurring after the first week (Fig. 1*e*). In Georgia, air temperature varied diurnally from 13 to 32 °C (Fig. 1*f*), and the maximum daily air temperature underneath the tarp consistently exceeded 50 °C for the first 12 days after fumigation (Fig. 1*h*). Soil temperature at 10 cm in depth in the water-sealed plots varied from 15 to 27 °C in Wisconsin and from 18 to 32 °C in Georgia (Figs. 1*e*, 1*f*). In the tarped plots, the soil temperatures ranged from 17 to 38 °C in Wisconsin (Fig. 1*g*) and from 23 to 38 °C in Georgia (Fig. 1*h*).

Methyl isothiocyanate emission from dazomet plots

In Wisconsin, MITC emissions from dazomet treatments were greater from tarped than from water-sealed plots (Table 2), and more than 95% of total emission occurred during the first week (Fig. 2). In the water-sealed area, lower amounts of MITC escaped from the plots treated with a rotary tiller than from those treated with a spading machine. The flux density was diurnally cyclic, and emissions were lower in the early morning than in the late afternoon to evening hours (Fig. 2*a*). Maximum flux density was 4.3 μg·m^{-2}·s^{-1} in the tarped plots; lower emissions were found for water-sealed plots where maximum flux density was 1.3 μg·m^{-2}·s^{-1}.

In Georgia, MITC emissions from dazomet plots were similar for both tarped and water-sealed plots (Table 2; Fig. 3). Emissions from all dazomet-treated plots in Georgia were higher than those found in Wisconsin ($P = 0.05$). Of the total emissions recorded for dazomet plots at the Georgia nursery, 55% and 89% of MITC losses occurred during the first 24 h from the tarped and water-sealed plots, respectively. When summed for the first week following chemical incorporation, 73% and 89% of the total MITC losses occurred in the tarped and water-seal treatments, respectively. Flux density during the first week was also diurnally cyclic, especially from the tarped plots (Fig. 3*a*). MITC emissions were greatest within 12 h after application for each chemical. The maximum flux densities were 9.2 and 14.7 μg·m^{-2}·s^{-1} for tarped and water-sealed plots, respectively.

Both the emission flux and the cumulative loss of MITC were greater in Georgia than in Wisconsin (Figs. 2 and 3; Table 2). Assuming that 100% of the applied dazomet converted to metam sodium (Kim et al. 1994) and that 90% of the metam sodium then converted to MITC (Smelt and Liestra 1974), the total air emissions of MITC per total molar equivalent MITC were less than 2.1% in Wisconsin and 4.7% in Georgia (Table 2).

Methyl isothiocyanate emissions from metam sodium plots

In Wisconsin, MITC flux densities from metam sodium treatments were similar for tarped and water-sealed plots ($P = 0.26$) (Table 2; Fig. 4*a*). From tarped plots, an average maximum flux density of 10.7 μg·m^{-2}·s^{-1} occurred 31.5 h after chemical application. The average maximum flux density reached 25.3 μg·m^{-2}·s^{-1} in the water-sealed plots only 3.5 h after application. As was found with MITC emissions from dazomet plots, the flux density from metam sodium plots was diurnally cyclic during the first 3 days, especially from the tarped plots

Fig. 1. Irrigation and precipitation (*a*, *b*), soil moisture (*c*, *d*), and soil and air (Tair) temperature (*e–h*) in forest nurseries at Hayward, Wisconsin, and Byromville, Georgia. Day after fumigation refers to the beginning of 6 August 2002 and 9 September 2003 for the Hayward and Byromville experiments, respectively.

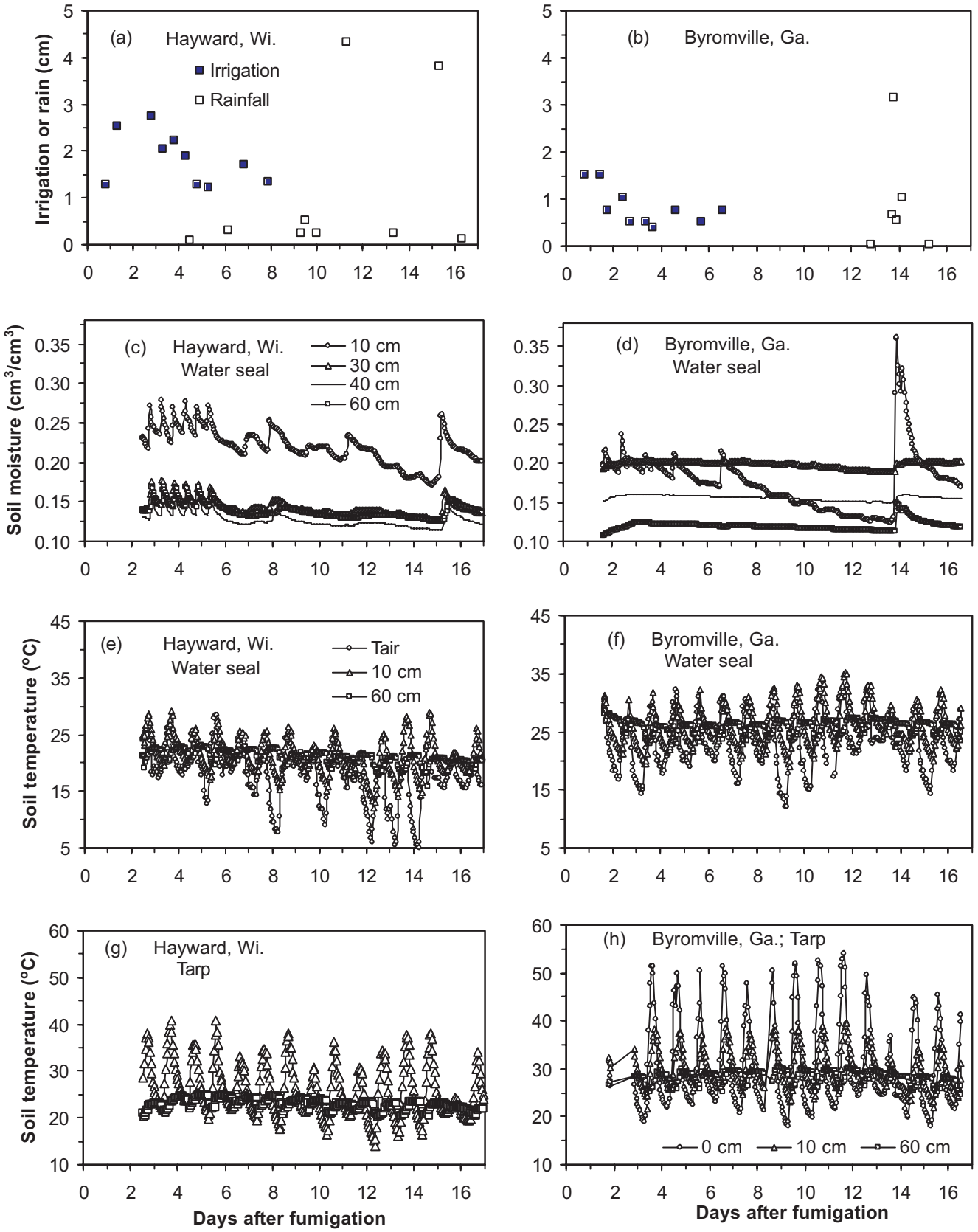


Table 2. Final cumulative emission loss of soil fumigants.

Chemical	Location	Final cumulative loss			
		Tarp (g/m^2)*	Water seal (g/m^2)*	Tarp (% of total applied)†	Water seal (% of total applied)†
Dazomet	Hayward, Wisconsin; spade	0.373±0.081aA	0.048±0.015bA	2.1	0.3
	Hayward, Wisconsin; tiller	ne	0.008±0.002B	ne	0.1
	Byromville, Georgia	1.062±0.196aB	0.727±0.184aC	4.7	3.2
Metam sodium	Hayward, Wisconsin	0.442±0.094aA	0.318±0.094aA	2.5	1.8
	Byromville, Georgia	0.922±0.305aB	0.203±0.046bA	5.2	1.1
Chloropicrin	Hayward, Wisconsin	1.600±0.219aA	3.718±0.551bA	9.5	22.1
	Byromville, Georgia	3.024±0.587aB	2.381±1.195aA	18.0	14.2

*Cumulative loss of methyl isothiocyanate (MITC) was measured for dazomet and metam sodium. Means ± standard errors are presented for four replications. Means with different letters within each chemical group are significantly different ($P \leq 0.05$) between the tarp and water-seal treatments for the same location (lowercase letters) or between experiment locations for the same cover treatment (uppercase letters). ne, not evaluated.

†Assumed on a molar basis 100% conversion from dazomet to metam sodium (Kim et al. 1994) and 90% conversion from metam sodium to MITC (Smelt and Leistra 1974).

Fig. 2. Emission flux density (*a*) and cumulative emission (*b*) of methyl isothiocyanate (MITC) after application of dazomet at Hayward, Wisconsin, from tarp and water-seal treatments. Application of dazomet was made on 7 August 2002 (day 0 represents 2400 h).

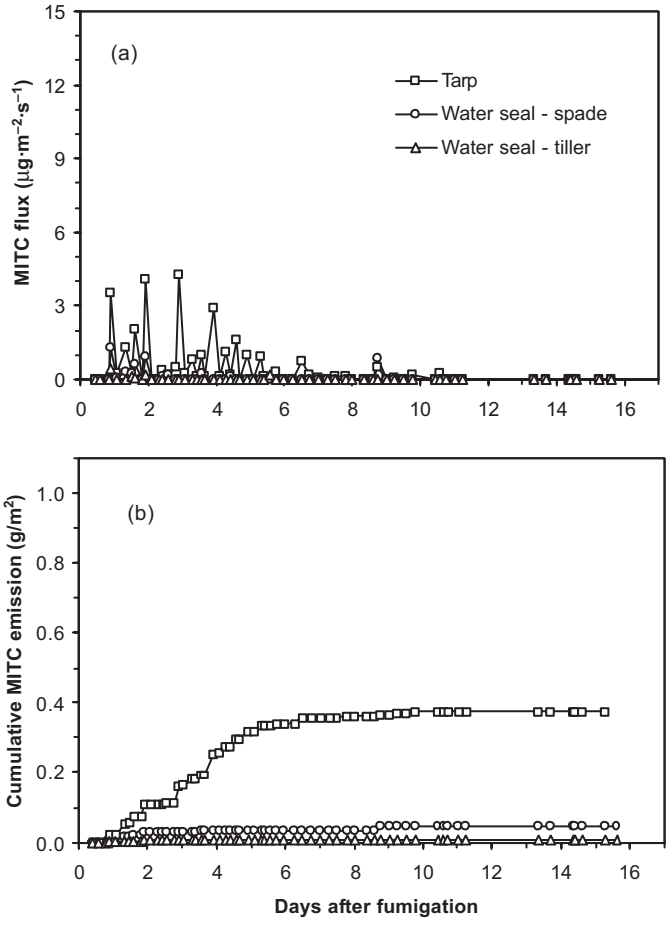
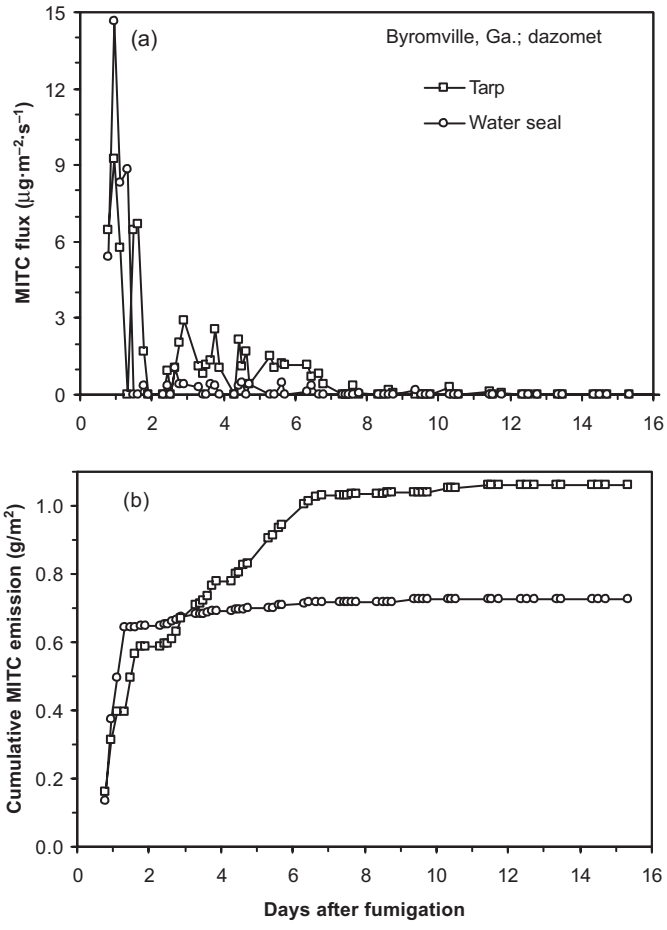


Fig. 3. Emission flux density (*a*) and cumulative emission (*b*) of methyl isothiocyanate (MITC) after application of dazomet at Byromville, Georgia, from tarp and water-seal treatments. Application of dazomet was made on 9 September 2003.



(Fig. 4*a*). Cumulative MITC emissions during this time period accounted for 72% and 98% of the total loss from tarped and water-sealed plots, respectively (Fig. 4*b*).

In Georgia, greater MITC air emissions from metam sodium treatments occurred in tarped than water-sealed plots (Table 2; Fig. 5). Average flux densities reach a maximum 12 h after metam sodium application in both surface treatment areas. The maximum flux density was 28.8 $\mu g \cdot m^{-2} \cdot s^{-1}$ for the tarped and 5.4 $\mu g \cdot m^{-2} \cdot s^{-1}$ for the water-sealed plots (Fig. 5*a*). Emission rates decreased quickly after initial large losses in

Fig. 4. Emission flux density (*a*) and cumulative emission (*b*) of methyl isothiocyanate (MITC) after application of metam sodium at Hayward, Wisconsin, from tarp and water-seal treatments. Application of metam sodium was made on 6 August 2002.

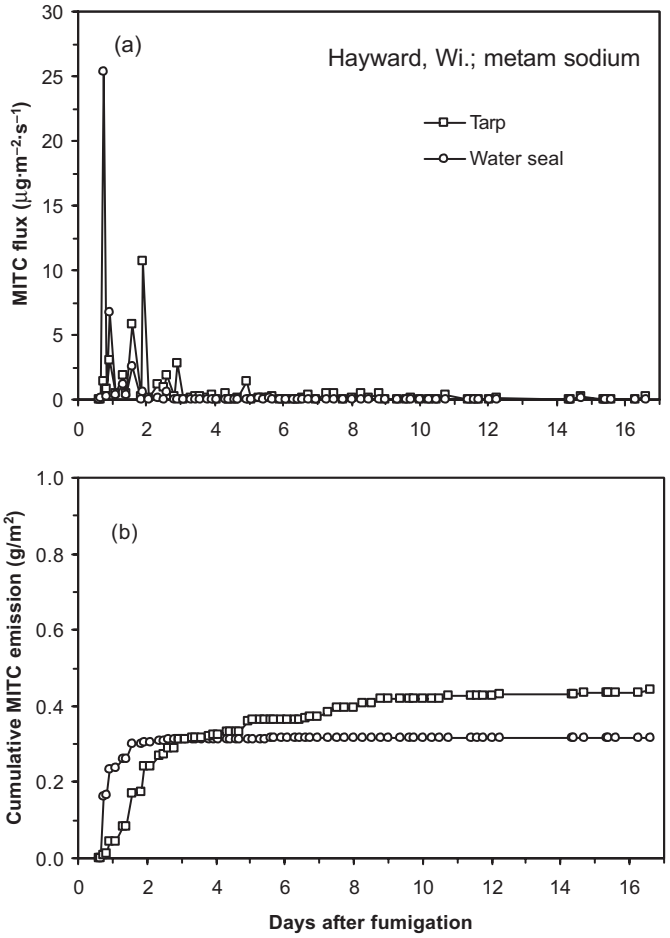
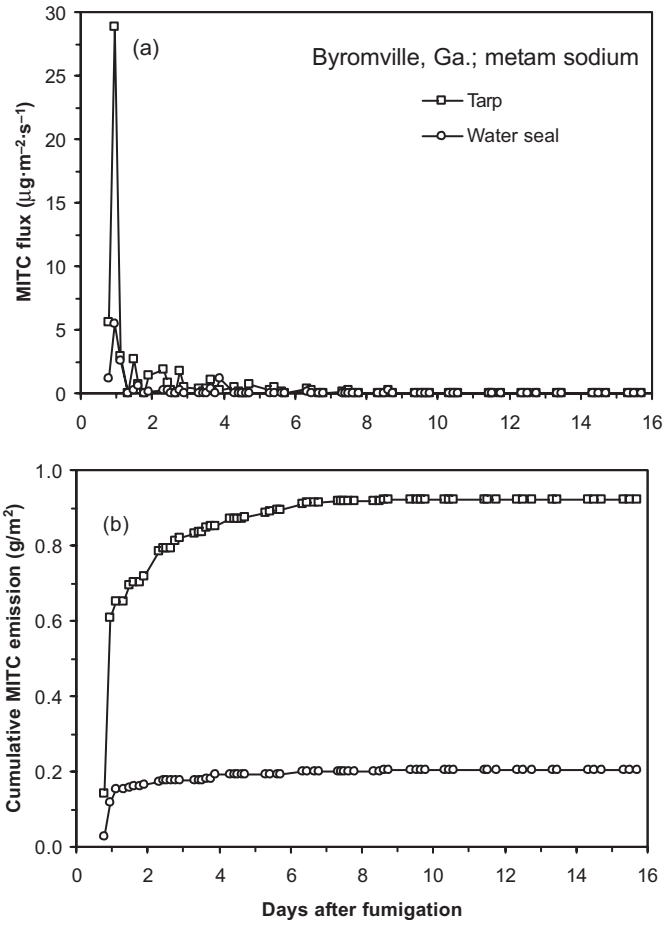


Fig. 5. Emission flux density (*a*) and cumulative emission (*b*) of methyl isothiocyanate (MITC) after application of metam sodium at Byromville, Georgia, from tarp and water-seal treatments. Application of metam sodium was made on 9 September 2003.



Georgia. Of the total emissions recorded for metam sodium plots, 76% and 80% of MITC losses occurred during the first 24 h from the tarped and water-sealed plots, respectively. Furthermore, 100% of the total MITC losses recorded for the tarped and 99% for the water-sealed plots occurred within the first 3 days after metam sodium application. Assuming that 90% of the metam sodium converted to MITC (Smelt and Liestra 1974), the total air emissions of MITC per total molar equivalent of MITC were less than 2.5% in Wisconsin and 5.2% in Georgia (Table 2).

Chloropicrin emissions

In Wisconsin, CP emissions were higher in the water-sealed than the tarped plots (Table 2; Fig. 6). Nearly all the emissions occurred in the first week when cumulative losses were 92% of the total for tarped and 98% for water-sealed plots. Flux density from CP plots was diurnally cyclic during the first week with lower fluxes occurring in the morning than in the afternoon or evening (Fig. 6*a*). Average maximum flux density reached 62.9 $\mu g \cdot m^{-2} \cdot s^{-1}$ in water-sealed plots 12 h after CP injection, while average maximum flux density in tarped plots (15.3 $\mu g \cdot m^{-2} \cdot s^{-1}$) occurred 31.7 h after injection.

In Georgia, flux densities from the CP treatment were similar for tarped and water-sealed plots ($P = 0.35$) (Table 2; Fig. 7). The rate of CP emissions was lower over time than that found in Wisconsin. Cumulative air emissions of CP during the first week after injection were 82% for tarped and 52% for water-sealed plots (Fig. 7*b*). There were no distinctive peaks for CP emissions in either the tarped or water-sealed plots. The maximum flux density ranged from 10 to 15 $\mu g \cdot m^{-2} \cdot s^{-1}$ during the first 44 h in the tarped plots, while maximum flux density averaged 8 $\mu g \cdot m^{-2} \cdot s^{-1}$ during the first 15 h after CP injection in the water-sealed plots (Fig. 7*a*). Final cumulative emission losses of CP were less than 22% of the actual CP applied in either location for either surface treatment (Table 2).

Discussion

The rate and temporal trend of MITC air emissions from plots receiving metam sodium were comparable to previously published findings where a solution formulation of metam sodium with an application method similar to ours was used (van den Berg et al. 1999). Emissions of CP in the present study were also comparable with computer simulation models for similar soil and environmental conditions (Wang and Knuteson 2001). Direct validation of our findings is not possible because of inherent limitations with the cham-

Fig. 6. Emission flux density (*a*) and cumulative emission (*b*) of chloropicrin (CP) at Hayward, Wisconsin, from tarp and water-seal treatments. Application of CP was made on 6 August 2002.

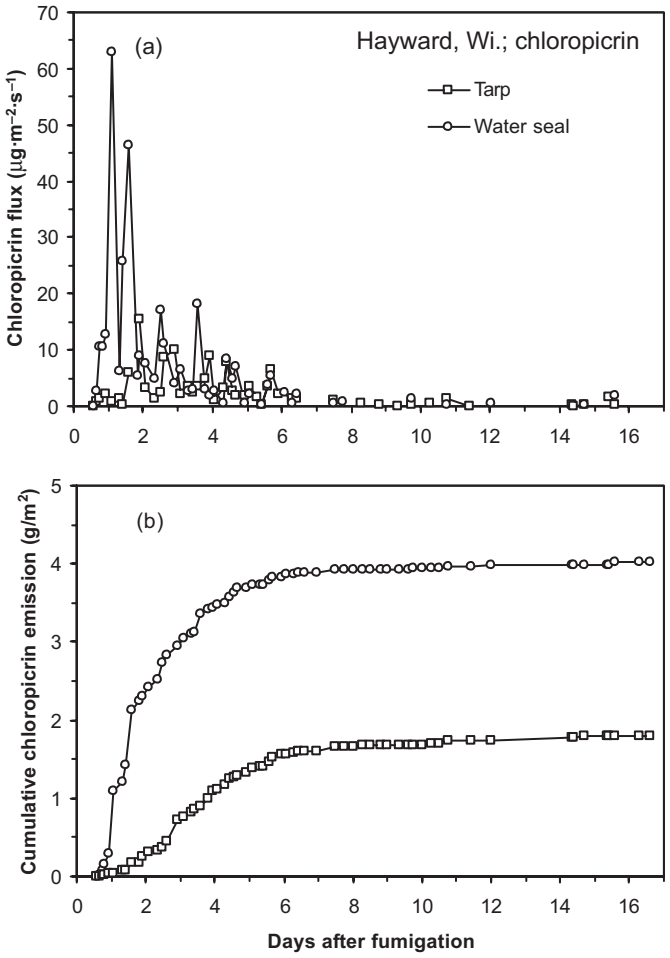
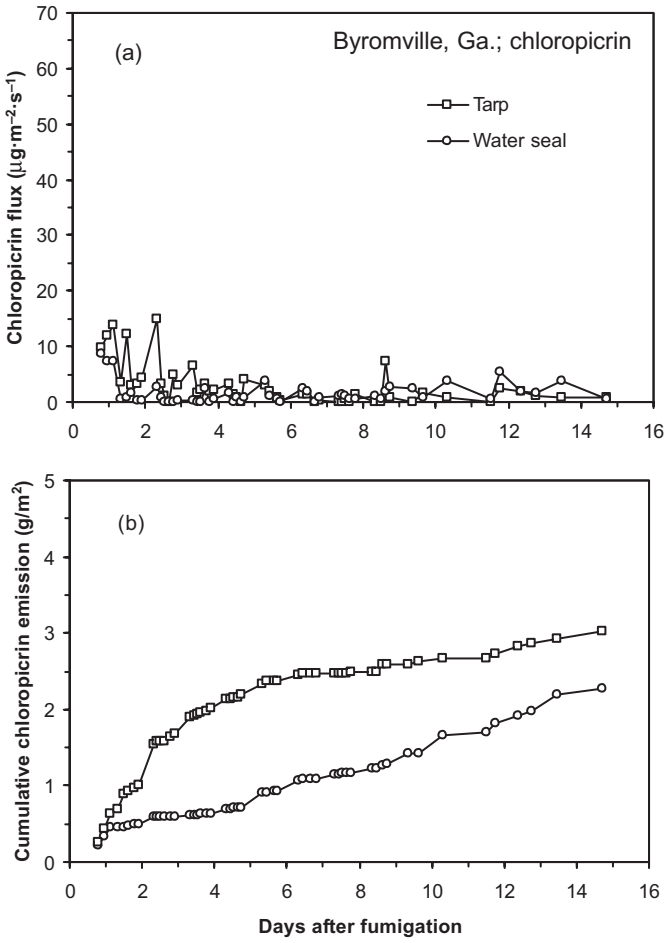


Fig. 7. Emission flux density (*a*) and cumulative emission (*b*) of chloropicrin (CP) at Byromville, Georgia, from tarp and water-seal treatments. Application of CP was made on 9 September 2003.



ber method; however, these comparisons provide an indirect validation of the emission measurements employed in this study.

The diurnal cyclic behavior in MITC or CP emissions that we observed can be explained by diurnal temperature variations. Rate of fumigant gas movement is directly related to temperature because of the positive relationship between gas diffusion and temperature (Wang et al. 2000). The higher emission fluxes during late afternoon and early evening hours occurred when the air or soil temperatures were at their daily maximum. Conversely, emissions were lowest in the morning when temperatures were at their daily minima (Figs. 1*e*–1*h*).

The method of fumigant delivery to the soil would be expected to affect air emissions of MITC and CP. Because the metam sodium was a liquid formulation that was sprayed on the soil surface and subsequently incorporated, it was not surprising that the majority of MITC emissions from these plots occurred within the first 3 days, regardless of surface containment treatment. The relatively slower rate of MITC emission in dazomet-treated plots (i.e., occurred over 1 week) is attributed to its granular formulation that was spread on the soil surface and subsequently incorporated, but required time for conversion from dazomet to metam sodium to MITC (Kim et al. 1994). Therefore, the time required for dissolution of dazomet granules by free soil water would delay MITC generation in dazomet plots compared with metam sodium plots. Although CP was a liquid, significant emissions occurred over a week, which was similar to the time frame for MITC emissions from dazomet-treated plots. The longer emission period and more gradual rate of emission for CP compared with metam sodium and its associated MITC generation was primarily attributed to the direct injection of CP to 20–25 cm in depth with no immediate exposure of the chemical near the soil surface. The relatively higher vapor pressure of CP compared with metam sodium may have also contributed to the longer emission period.

In this study, the final cumulative MITC emission losses accounted for a very small percentage of the equivalent MITC applied as either dazomet or metam sodium (Table 2). Accelerated rates of MITC degradation in the soil may have led to the very low levels of overall gas emissions. MITC degradation in soil is affected by several factors including prior soil treatments with metam sodium and soil temperature. MITC degrades faster after repeated application of metam sodium in soil (Smelt et al. 1989), and in a recent laboratory study, repeated metam sodium or dazomet application reduced the MITC half-life to 5–30 h depending on the soil type (Di Primo et al. 2003). Higher MITC (and CP) degradation rates are also correlated with higher temperatures (Gan et al. 1999,

2000). Based on these earlier studies, the low MITC emissions found at Wisconsin nursery may be partly attributable to the history of soil fumigation with MITC products at this nursery. Furthermore, the low MITC emissions found at the Georgia nursery may be partly attributable to the relatively high soil temperatures during the study.

A number of factors may affect air emissions of soil fumigant gases through different surface containment treatments. For tarp treatments, the permeability of polyethylene covers to soil fumigants is dependent on temperature and gas concentrations. Wang et al. (1997*b*, 1998*b*) reported increased permeability at higher temperatures based on field studies with methyl bromide. In the tarped plots of our study, cumulative MITC or CP emissions in Georgia were about twice the levels found in Wisconsin. Daily air temperatures were about 8 °C higher during treatment in the southern nursery compared with the northern one. Furthermore, polyethylene tarps have been shown to be relatively inefficient for containing MITC (Yates et al. 1996*b*). At both nurseries in the present study, cumulative MITC emissions (generated from dazomet and metam sodium) were generally greater and occurred over a longer duration in tarped plots than those that were water sealed.

Differences observed for MITC emissions from the water-sealed plots were attributed to differences in effective incorporation depth, chemical rate, and amount of daily irrigation water used to maintain the surface seal. The short duration of MITC emissions from metam sodium and dazomet plots is likely due, in part, to accelerated transformation of product to MITC (by hydrolysis) and chemical percolation to greater soil depths caused by daily watering. Because of the relatively large amount of irrigation water applied in Wisconsin plots, the shallower incorporation depth for the tiller versus the spading machine did not increase MITC emission. On the contrary, MITC emissions were actually lower in plots treated with the tiller compared with those treated with the spading machine. This was most likely due to differences in chemical rate used in spading machine-treated plots (448 $kg \cdot ha^{-1}$) and tiller-treated plots (336 $kg \cdot ha^{-1}$). Overall, MITC emissions were lower in the Wisconsin plots than in the counterpart plots at the Georgia nursery. Differences in the amounts of irrigation water used at the two nurseries are believed to be the main reason for this difference.

In this study, we observed no foliar damage to seedling crops or cover crops growing in areas adjacent to study plots at either nursery. In previously reported instances of crop damage (Texas, Oregon, and Washington) that occurred in areas adjacent to fields fumigated with dazomet or metam sodium, tarps or water seals were not used to contain the fumigants (Buzzo 2003; per Carey 2000*a*; Scholtes 1989). The method of fumigant application in these situations ranged from surface application followed by rotary tiller incorporation, shank injection, or both. The soil surface was compacted (rolled in at least two of these situations, but methods were not clearly stated in the other published account). Lastly, still air events or temperature inversions occurred immediately after fumigation in the Oregon and Washington cases, and the lateral surface transport of phytotoxic concentrations of atmospheric emissions of the fumigant gases to adjacent crop fields were cited as key factors in both situations (Scholtes 1989; Buzzo 2003). MITC is known to be toxic to growing plants, especially in closed areas (Information Ventures Inc. 2004*a*). However, the exact concentrations and exposure times that lead to death or sublethal damage to plants are not known. The concentrations and surface atmospheric conditions in the above-mentioned damage situations were not measured, but were obviously sufficient to cause both foliar damage and seedling death. In our study, a very small percentage (<5%) of the equivalent MITC was lost through atmospheric emission among all treatments. Furthermore, less MITC emission occurred in the water-sealed plots compared with the tarped plots. The daily irrigation used to maintain the water seal was probably an important factor related to low levels of MITC emissions. The effect of such low concentrations of MITC on seedling health requires additional study under controlled conditions.

MITC and CP air emissions following fumigation also may potentially affect health of nearby nursery workers or building inhabitants. Exposure to low concentrations of dazomet can cause skin and eye irritation; the probable oral lethal dosage is 50–500 $mg \cdot kg^{-1}$ (Information Ventures Inc. 2004*a*). Human exposure to low CP concentrations can cause eye, nose, and throat irritations, but no information is available on lethal or sublethal toxic dosages (Information Ventures Inc. 2004*b*). During our study, maximum MITC emissions were 14.7 and 28.8 $\mu g \cdot m^{-2} \cdot s^{-1}$ after dazomet and metam sodium applications, respectively, at the Georgia site. At the higher emission rate and assuming no atmospheric mixing (i.e., very still conditions), it would take 60–600 h to fill a 1.8-m^3 air column with 3.5–35 g MITC, which is regarded as the lethal dose for a 70-kg human in an equivalent space. For CP at the maximum emission rate observed in this study (62.9 $\mu g \cdot m^{-2} \cdot s^{-1}$ in Wisconsin) it would take 950 h to fill a 1.8-m^3 air column to a concentration of 120 $mg \cdot L^{-1}$, which is considered to be a lethal level for a mammal the size of a rabbit. Thus, it seems unlikely that emissions measured in our study posed a lethal threat to humans near the fumigated sites. However, it is not known what CP and MITC concentrations and exposure times can lead to sublethal toxic responses in humans.

In summary, this is the first report on levels of MITC and CP escaping to the atmosphere through tarps or water-sealed surfaces following fumigation in forest nurseries. A very small percentage of the applied equivalent of MITC was lost through either surface treatment, and lower emissions occurred with the water seal. Cumulative emission of CP accounted for 10%–20% of the applied CP. Over 70% of cumulative emissions for both MITC and CP occurred within 1 week of application. Although either surface containment treatment can be used by nursery managers to reduce the risk of damage to nearby seedling crops or harm to humans due to chemical emissions, the water-seal treatment appears to be slightly more effective than tarps for reducing these emissions.

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