

# Fumigant distribution in forest nursery soils under water seal and plastic film after application of dazomet, metam-sodium and chloropicrin

Dong Wang,<sup>1\*</sup> Stephen W Fraedrich,<sup>2</sup> Jennifer Juzwik,<sup>3</sup> Kurt Spokas,<sup>1</sup> Yi Zhang<sup>1</sup> and William C Koskinen<sup>4</sup>

<sup>1</sup>Department of Soil, Water, and Climate, University of Minnesota, St Paul, MN, USA

<sup>2</sup>USDA-Forest Service, Southern Research Station, Athens, GA, USA

<sup>3</sup>USDA-Forest Service, North Central Research Station, St Paul, MN, USA

<sup>4</sup>USDA-ARS, Soil and Water Management Unit, St Paul, MN, USA

**Abstract:** Adequate concentration, exposure time and distribution uniformity of activated fumigant gases are prerequisites for successful soil fumigation. Field experiments were conducted to evaluate gas phase distributions of methyl isothiocyanate (MITC) and chloropicrin (CP) in two forest-tree nurseries. Concentrations of MITC and CP in soil air were measured from replicated microplots that received dazomet, metam-sodium and CP. Half of the plots were covered with high-density polyethylene tarp immediately after fumigation; the other half were not covered but received daily sprinkler irrigation for 1 week to create and maintain a water seal. The magnitude of MITC concentrations was similar between nurseries for metam-sodium in both tarp and water seal treatments and for dazomet in the tarp treatment. Consistently greater MITC and CP concentrations were found in the upper 30 cm of soil in the tarped plots compared with the water-sealed plots. Despite potential environmental and economic benefits with the water seal method, tarp covers were more reliable for achieving and maintaining higher MITC and CP concentrations and less prone to variations due to irrigation/rain, soil bulk density and other environmental conditions.

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**Keywords:** methyl isothiocyanate; chloropicrin; dazomet; metam-sodium; fumigation; soil gas concentration

## 1 INTRODUCTION

Soil fumigation is an important management practice in forest-tree nurseries for controlling soil-borne plant pathogens, weeds and plant parasitic nematodes.<sup>1</sup> Methyl bromide and chloropicrin (CP) were the most commonly used soil fumigants in US forest-tree nurseries in the 1990s.<sup>1</sup> However, bromine resulting from breakdown of volatilised methyl bromide contributes to loss of the Earth's stratospheric ozone layer,<sup>2</sup> and methyl bromide for use as a soil fumigant is scheduled to be phased out in 2005. In the meantime, exemptions are being proposed on a yearly basis for some crops, including forest-tree seedlings, because of perceived problems with available alternatives.

Dazomet, metam-sodium and CP have been used for soil fumigation in forest-tree nurseries either individually or in some combination in order to achieve

a broad-spectrum pest control similar to that of the methyl bromide/CP combination. Dazomet and metam-sodium are precursors for methyl isocyanate (MITC), which is the primary active ingredient responsible for pest mortality. Dazomet, when used alone, is effective against a number of soil-borne nursery plant pathogens.<sup>3,4</sup> In field trials conducted in several nurseries, a co-application of metam-sodium and CP was found to be as effective for seedling production as methyl bromide/CP.<sup>5</sup> The metam-sodium/CP combination was also found to possess one of the highest pesticidal efficacies against yellow nutsedge tubers (*Cyperus esculentus* L.) compared with other fumigant combinations tested, including methyl bromide/CP, methyl iodide/CP, 1,3-dichloropropene/CP, propargyl bromide/CP and CP alone.<sup>6</sup> Comparative efficacy studies have been carried out using CP alone in forest-tree nursery fumigation trials.<sup>7</sup>

\* Correspondence to: Dong Wang, Department of Soil, Water, and Climate, University of Minnesota, 1991 Upper Buford Circle, St Paul, MN 55108, USA

E-mail: wangd@umn.edu

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A key factor that contributes to successful fumigation is achieving a uniform fumigant distribution in the targeted soil profile. Gas diffusion is the primary mechanism for fumigant movement in soil. In contrast to methyl bromide, which is a gas with a boiling point of 4.5 °C under ambient pressure, the boiling point of MITC is 119 °C<sup>8</sup> and of CP 112 °C.<sup>9</sup> Most alternative fumigants also have much lower vapour pressure values than methyl bromide. The vapour pressure of methyl bromide is 188.8 kPa, but the values for MITC and CP are only 2.1 kPa<sup>8</sup> and 3.2 kPa<sup>9</sup> respectively. The dispersal rate of a fumigant and its persistence at high concentrations are important factors in the selection process for alternative fumigants.

To increase pesticidal efficacy and reduce atmospheric emissions, fumigated fields are usually covered with plastic tarps immediately after treatment. Because of problems associated with tarp cost and subsequent disposal, other methods of surface cover, if effective, would be preferable. For dazomet, sprinkler irrigation is recommended by the manufacturer as a means of activating the chemical and providing a surface seal.<sup>10</sup> In this paper we report findings on MITC and CP concentrations in soil air from two forest-tree nurseries following application of dazomet, metam-sodium and CP under either tarp or water seal covers.

## 2 MATERIALS AND METHODS

### 2.1 Site and microplot description

Fumigation experiments were conducted on microplots at two forest-tree nurseries to determine the distribution of MITC and CP in soil air following application of dazomet, metam-sodium and CP. The first experimental site was at the Wisconsin Hayward State Forest Nursery (46.0 °N, 91.5 °W) located near Hayward, WI, and the second site was at the Flint River Nursery (32.2 °N, 84.0 °W) near Byromville, GA. Both nurseries have routinely fumigated soil in support of bare-root seedling production. The soil at the Hayward nursery is a Vilas loamy sand (sandy, mixed, frigid, Entic Haplorthod) containing 88.0% sand, 5.7% silt and 6.3% clay in the upper 0–30 cm layer. Total organic carbon in the soil was 1.1%, the pH was 6.8 measured in 1:1 water slurry, and bulk density was 1.61 g cm<sup>-3</sup>. The soil at the Byromville nursery is a Eustis loamy sand (siliceous, thermic, Psammentic Paleudult) containing 86.0% sand, 7.1% silt and 6.9% clay in the upper 0–30 cm layer. Other soil properties at the site were 1.9% of total organic carbon, pH of 5.6 and bulk density of 1.36 g cm<sup>-3</sup>.

At each nursery, two study areas were established. In each study area the fumigant treatments were dazomet and a co-application of metam-sodium and CP. In one study area the treatment plots were water sealed, while plots in the other area were tarped with high-density polyethylene plastic. The experimental design in each study area was a randomised complete block with two treatments and four replications. The dimensions

of these microplots were 2.4 m wide by 9.1 m long separated by a 9.1 m buffer space between plots.

During each experiment, soil temperature and moisture were measured at multiple depths using an automated thermocouple and time domain reflectometry (TDR) system.<sup>11</sup> Wind speed and air temperature data were obtained from weather stations located at or near the two nurseries.

### 2.2 Fumigant application

Granular dazomet (Basamid<sup>TM</sup>, BASF) was applied on 7 August 2002 at the Wisconsin nursery. A tractor-drawn drop spreader was used to apply the granules to the soil surface at 448 kg ha<sup>-1</sup>, followed by soil incorporation to a maximum depth of 20 cm with a spading machine.<sup>12</sup> Soil moisture content at the time of fumigant application was 0.16 and 0.23 cm<sup>3</sup> cm<sup>-3</sup> in the tarp and water seal plots respectively. At the Georgia nursery, dazomet was applied on 9 September 2003 at 560 kg ha<sup>-1</sup> with a hand-operated drop spreader, followed by soil incorporation to a maximum depth of 20 cm with a roto-tiller.<sup>13</sup> Soil moisture content at the time of fumigant application was 0.12 cm<sup>3</sup> cm<sup>-3</sup> in both the tarp and water seal plots.

Metam-sodium 0.5 kg litre<sup>-1</sup> SL (Vapam HL<sup>TM</sup>, AMVAC) was applied on 6 August 2002 at the Wisconsin nursery by spraying the solution at 686 litres ha<sup>-1</sup> over the soil surface, followed immediately by incorporation to a maximum depth of 12 cm with a roto-tiller. Within minutes, CP was injected at 20–25 cm depth at 168 kg ha<sup>-1</sup>, followed by a bed roller to seal off the shank traces. Soil moisture content at the time of fumigant application was 0.16 cm<sup>3</sup> cm<sup>-3</sup> in both the tarp and water seal plots. Irrigation (~1.3 cm of water) was applied to the metam-sodium/CP water seal plots after fumigant application. Subsequent irrigation was applied on 7 August after dazomet application and on the following 6 days. At the Georgia nursery, metam-sodium and CP were applied on 9 September 2003 using the same procedures and application rates as used at the Wisconsin nursery, but the roto-tiller for metam-sodium incorporation was the same as for dazomet incorporation, which reached 20 cm depth in the soil. Because of a faulty regulator and fumigant leakage on the rig, the CP injection (to 20–25 cm depth) was delayed 3 h after metam-sodium application, and the actual amount of CP injected into the soil was most likely less than the 168 kg ha<sup>-1</sup> target rate. Soil moisture content at the time of fumigant application was 0.12 cm<sup>3</sup> cm<sup>-3</sup> in both the tarp and water seal plots. About 1.5 cm of water was applied immediately after CP injection to the water seal plots, and subsequent irrigation was applied on the following 6 days. 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 on days 4–7) were based on the manufacturer's recommendation for dazomet,<sup>10</sup> and the same irrigation regimes were

used for all water seal plots during both experiments. Whereas the high-density polyethylene tarp (1 mil or 0.025 mm, manufactured by Cadillac Plastics, Inc., per Hendrix and Dail, Inc., Cairo, GA, USA) was laid by the fumigation rig in the metam-sodium/CP plots immediately following CP injection, all dazomet plots were covered manually with the same tarp and the edges were sealed with soil.

### 2.3 Soil air sampling

Multi-port soil air sampling probes were built before the experiments to facilitate measurement of MITC and CP concentrations in the soil. The probes were made with 125 cm long aluminium pipes (o.d. 3.45 cm, i.d. 2.54 cm) fitted with ten Teflon tubes (o.d. 1.8 mm, i.d. 0.71 mm). The first eight tubes were installed at 5 cm intervals beginning at 60 cm from the top of the pipes, and the ninth and tenth tubes were placed at distances of 105 and 120 cm from the top of the pipes respectively. Teflon tubing was fitted through perpendicular drilled holes (1.8 mm diameter) in the pipe wall and routed up the centre of the pipes. Tubing ends were trimmed flush to the outside edge of the aluminium pipe, and the other ends were mated at the surface with a quick connect (Small Parts, Inc., Miami Lakes, FL, USA). The pipes were filled with concrete to secure the tubing. The bottom ends of the aluminium pipes were fitted with a tapered tip, machined to 60° angle, to facilitate installation. One probe was installed at the centre of every fumigation plot and driven into the soil with a post driver. Care was taken to ensure that the opening of the first Teflon tube on each pipe was flush with the soil surface in order that the ten sampling ports were located at soil depths of 0, 5, 10, 15, 20, 25, 30, 35, 45 and 60 cm.

A ten-port soil air sampler designed similarly to that of Wang and Yates<sup>14</sup> was constructed and used for simultaneously withdrawing air samples from each of the ten Teflon tubes on the aluminium sampling probes. To capture sufficient MITC and CP in the soil air during each sampling event, 60 ml of air was drawn from each port through activated charcoal tubes for MITC and through polymer-based XAD tubes for CP (Supelco Inc., Bellefonte, PA, USA), which sorbed the fumigants. The sample tubes were stored in an ice chest prior to and during transport to the laboratory for analysis. To adequately document fumigant dispersion over time, 12 sampling events for the dazomet and 13 for the metam-sodium/CP plots were made during the course of the Wisconsin experiment at various elapsed times from 0.14 to 19.83 days after fumigant application. During the Georgia experiment, nine sampling events were made for dazomet and metam-sodium/CP from 0.18 to 16.69 days. A total of over 5000 soil air samples were obtained from the two field studies. MITC and CP concentrations of six sampling events from each experiment are presented to illustrate the dynamic processes of fumigant gas dispersion in these two nursery soils.

### 2.4 Analytical procedures for MITC and CP

The amount of MITC and CP on charcoal or XAD tubes was quantified using a Hewlett Packard (Atlanta, GA) 5890A gas chromatograph (GC) with an electron capture detector (ECD) and a nitrogen/phosphorus detector (NPD) connected to a Hewlett Packard HP-7694 headspace autosampler. 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, PA, USA) was used for MITC with a flow rate of 5 ml min<sup>-1</sup>, and a 30 m × 0.53 mm × 3 µm RTX-624 capillary column (Restek Corp.) was used for CP with a flow rate of 5 ml min<sup>-1</sup>. For MITC analysis the entire contents of each charcoal tube were transferred into a 21 ml headspace vial. After adding 2 ml of ethyl acetate, the vial was immediately capped with a Teflon-lined butyl rubber septum and crimped with an aluminium seal. The amounts of MITC in the vials were quantified using the NPD. The oven was held at 90 °C for 7 min and the NPD was at 220 °C. The response of the NPD 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 with the standards. A calibration check standard was added for every 30 samples. The detection limit of MITC was 0.01 µg, which corresponded to 0.17 mg m<sup>-3</sup> for a 60 ml sample. All vials were held at -20 °C until analysis and were analysed within 2 days after extraction. Similar procedures were used for CP, except that 2 ml of benzyl alcohol was added to each vial as the solvent, and the amount of CP was quantified using the ECD. The oven was held at 70 °C for 7 min and the ECD was at 250 °C. The response of the ECD 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.

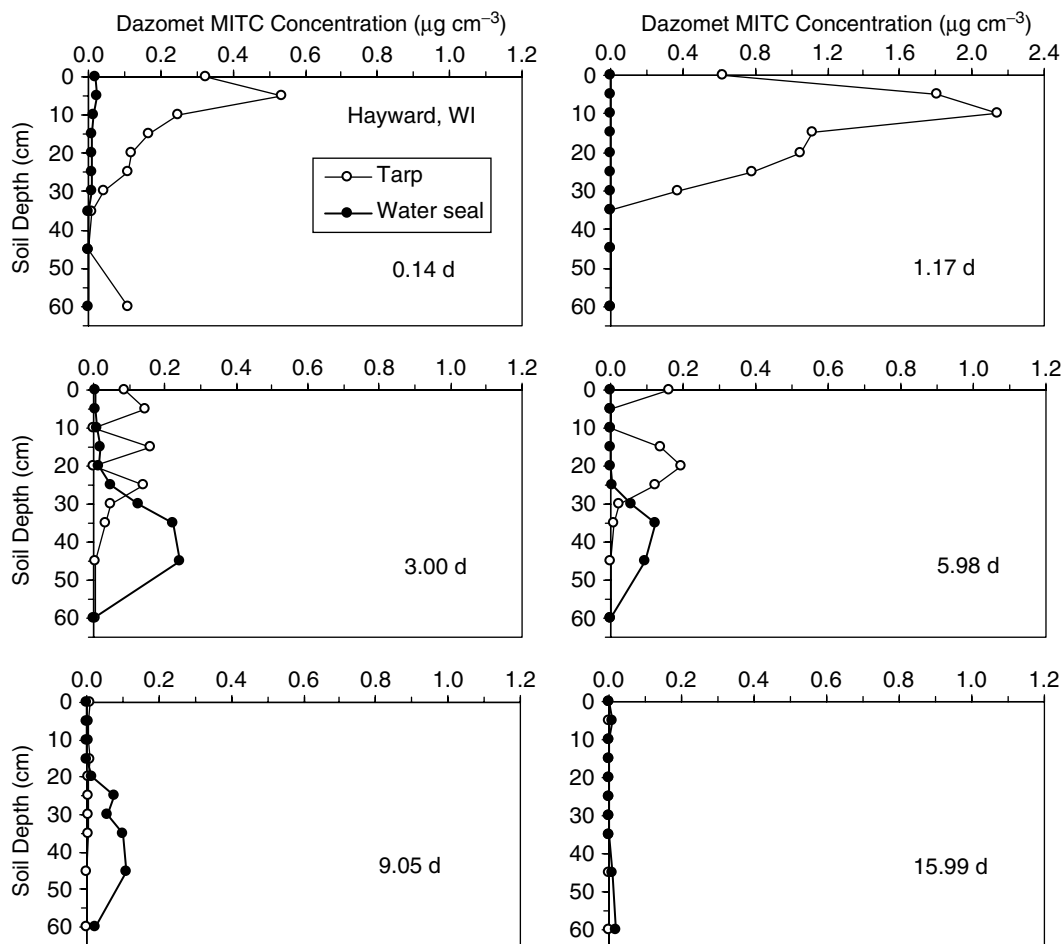
### 2.5 Statistical analysis

Comparisons were made between surface cover methods and field locations for average MITC and CP concentrations in the upper 30 cm of soil during the first 3 days after fumigant application. Because only four replications were used for each treatment, Student's *t*-test for small sample sizes was used for the statistical analysis.

## 3 RESULTS

### 3.1 MITC concentrations from dazomet

Up to 1.17 days after application, MITC concentrations in soil air in the dazomet treatment of the Wisconsin experiment were much higher in the tarped than in the water-sealed plots, where MITC was nearly undetectable throughout the soil profile (Fig. 1). The maximum MITC concentration was 2.14 µg cm<sup>-3</sup>, which occurred at 10 cm depth in the tarped plots at 1.17 days after fumigation. Although MITC concentrations decreased over time in the tarped plots,



**Figure 1.** Average concentrations of methyl isothiocyanate (MITC) in soil air at 0.14, 1.17, 3.00, 5.98, 9.05 and 15.99 days (d) after application of dazomet at Hayward, WI on 7 August 2002.

they increased at soil depths of 25–60 cm in the water-sealed plots at 3 days after fumigation and persisted until day 9. MITC had completely disappeared at all depths by day 9 in the tarped plots and by day 16 in the water-sealed plots.

During the Georgia experiment, MITC concentrations were also much higher in the tarped than in the water-sealed plots, but, unlike in the Wisconsin experiment, a significant amount of MITC was observed in the upper 45 cm soil profile of the water-sealed plots during the first day after application (Fig. 2). The highest MITC concentration,  $1.17 \mu\text{g cm}^{-3}$ , was found at 5 cm depth in the tarped plots at 0.30 days after fumigation. MITC concentrations decreased gradually over time in both the tarped and water-sealed plots. Similar to observations at the Wisconsin nursery, significant amounts of MITC were still present in the water-sealed plots at about 10 days after fumigant application.

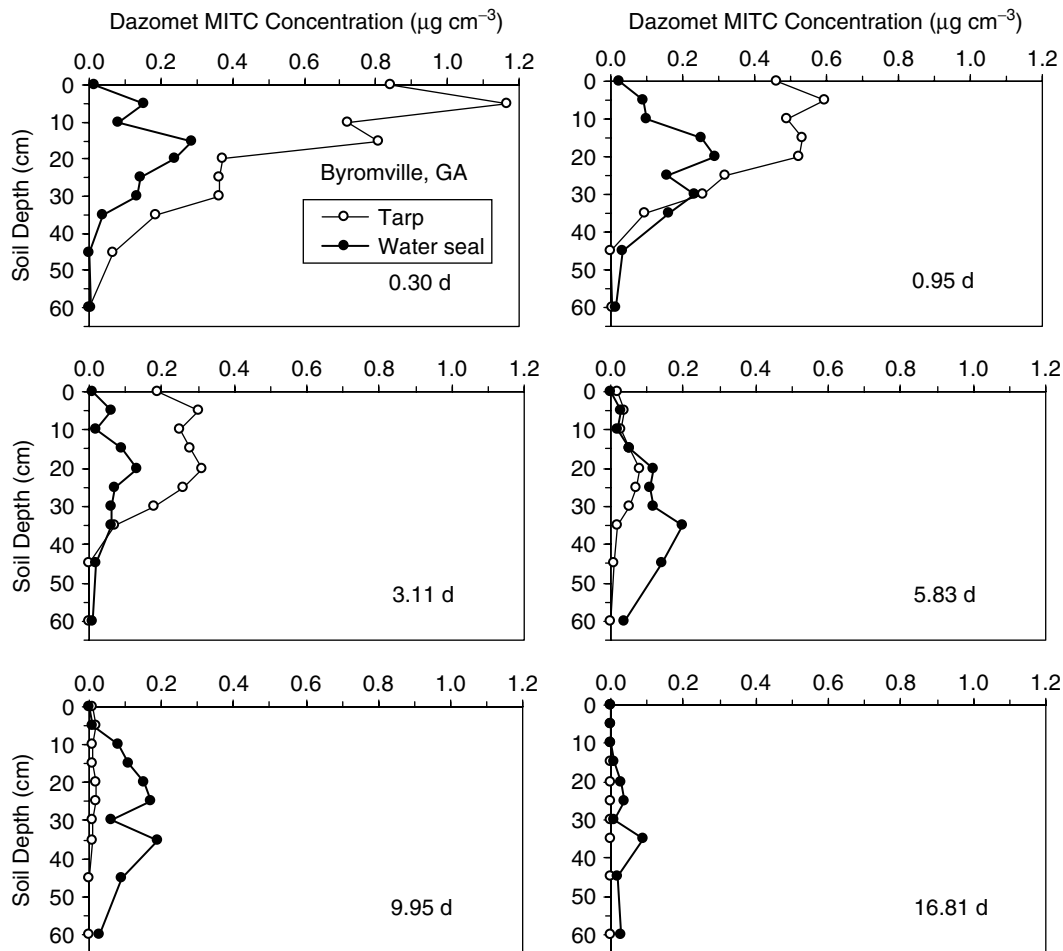
Average MITC concentrations in the upper 30 cm soil profile during the first 3 days after dazomet application were greater ( $P = 0.05$ ) in the tarped than in the water-sealed plots at both the Wisconsin and Georgia nurseries (Table 1). While the average concentrations were similar in the tarped plots at

the two nurseries ( $0.43$  vs  $0.42 \mu\text{g cm}^{-3}$ , Table 1), in the water-sealed plots the MITC concentrations were significantly greater at the Georgia nursery than at the Wisconsin nursery.

### 3.2 MITC concentrations from metam-sodium

MITC concentrations from metam-sodium during the first day at the Wisconsin nursery were greater in the upper 25 cm soil profile in the tarped than in the water-sealed plots (Fig. 3). The maximum average MITC concentration was again found in the tarped plots but never exceeded  $0.5 \mu\text{g cm}^{-3}$ . MITC concentrations decreased to near  $0 \mu\text{g cm}^{-3}$  in both the tarped and water-sealed plots at only 5.82 days after application. Unlike dazomet, significant MITC was found in the water-sealed plots during the first day after applying metam-sodium.

At the Georgia nursery, MITC concentrations were much higher in the tarped than in the water-sealed plots at 0.30 days after metam-sodium application (Fig. 4). MITC concentrations were similar in the tarped and water-sealed plots on days 0.95 and 3.11. While mean MITC concentrations in the upper 30 cm of soil were identical for the two surface cover methods at 5.83 days, much higher MITC values were measured at lower depths in the water-sealed



**Figure 2.** Average concentrations of methyl isothiocyanate (MITC) in soil air at 0.30, 0.95, 3.11, 5.83, 9.95 and 16.81 days (d) after application of dazomet at Byromville, GA on 9 September 2003.

**Table 1.** Average fumigant concentrations ( $\mu\text{g cm}^{-3}$  ( $\pm\text{SEM}$ );  $n = 117$ ) in the upper 30 cm soil profile during the first 3 days after application under tarp or water seal covers<sup>a</sup>

Chemical	Location	Surface cover method <sup>b</sup>	
		Tarp	Water seal
Dazomet	Hayward, WI	0.43 ( $\pm 0.05$ ) a A	0.04 ( $\pm 0.01$ ) b A
	Byromville, GA	0.42 ( $\pm 0.02$ ) a A	0.12 ( $\pm 0.01$ ) b B
Metam-sodium	Hayward, WI	0.12 ( $\pm 0.01$ ) a A	0.06 ( $\pm 0.01$ ) b A
	Byromville, GA	0.17 ( $\pm 0.01$ ) a A	0.09 ( $\pm 0.01$ ) b A
Chloro-picrin	Hayward, WI	4.30 ( $\pm 0.26$ ) a A	1.33 ( $\pm 0.13$ ) b A
	Byromville, GA	0.51 ( $\pm 0.04$ ) a B	0.19 ( $\pm 0.02$ ) b B

<sup>a</sup> Values with different letters within each chemical group are significantly different ( $P \leq 0.05$ ) between the tarp and water seal covers for the same location (lowercase letters) or between experiment locations for the same cover treatment (uppercase letters).

<sup>b</sup> Methyl isothiocyanate (MITC) was measured for dazomet and metam-sodium.

plots. Insignificant amounts of MITC were found at sampling times after 9.95 days.

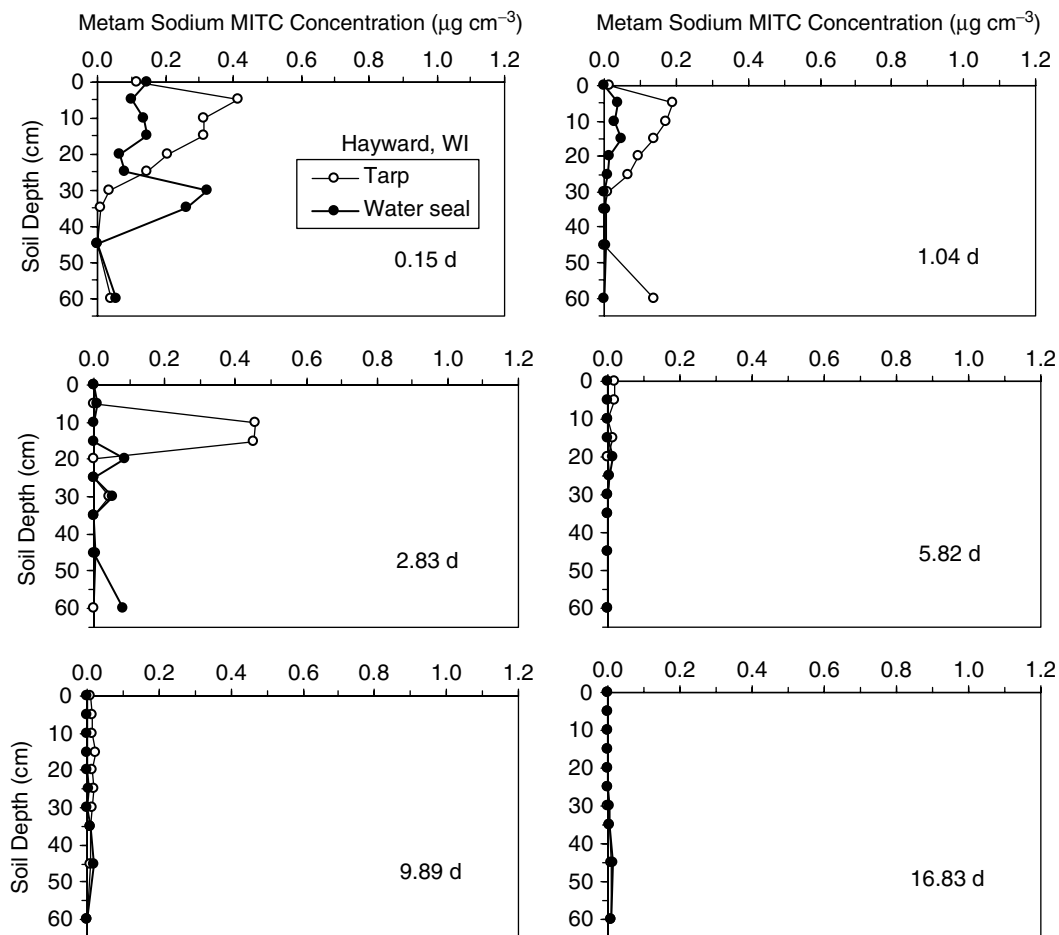
Similar to dazomet, average MITC concentrations in the upper 30 cm soil profile of the metam-sodium treatment were significantly greater in the tarped than in the water-sealed plots at both the Wisconsin and

Georgia nurseries during the first 3 days (Table 1). However, no significant differences were found in average MITC concentrations between the two field locations when comparing for the same surface cover method.

### 3.3 CP concentrations

The maximum CP concentration ( $11.4 \mu\text{g cm}^{-3}$ ) occurred in the tarped plots at 25 cm depth during the first sampling event (0.15 days) at the Wisconsin nursery (Fig. 5). Similar to observations made for MITC, CP values were greater in the tarped than in the water-sealed plots during the first day after CP injection. CP concentrations decreased gradually to  $\sim 0 \mu\text{g cm}^{-3}$  in both the tarped and water-sealed plots at 9.89 days after CP application.

Although CP concentrations were greater in the tarped than in the water-sealed plots during the first day at the Georgia nursery, the absolute CP values were much lower ( $\leq 1.7 \mu\text{g cm}^{-3}$ , Fig. 6) than those of the Wisconsin experiment. While CP in the tarped plots gradually decreased to  $\sim 0 \mu\text{g cm}^{-3}$  by 5.71 days after application, an increase in CP below 30 cm depth was observed in the water-sealed plots, reaching a maximum of  $2.7 \mu\text{g cm}^{-3}$  at 9.83 days. A significant



**Figure 3.** Average concentrations of methyl isothiocyanate (MITC) in soil air at 0.15, 1.04, 2.83, 5.82, 9.89 and 16.83 days (d) after application of metam-sodium at Hayward, WI on 6 August 2002.

amount of CP still remained in the lower soil profile in the water-sealed plots at 16.69 days after injection.

Similar to observations made for MITC, average CP concentrations in the upper 30 cm soil profile were significantly greater in the tarpred than in the water-sealed plots at the Wisconsin and Georgia nurseries during the first 3 days after CP application (Table 1). Because of the mechanical malfunctions, significantly lower CP concentrations were found in the Georgia nursery than in the Wisconsin nursery for both surface cover methods.

### 3.4 Wind speed, air and soil temperature and soil moisture

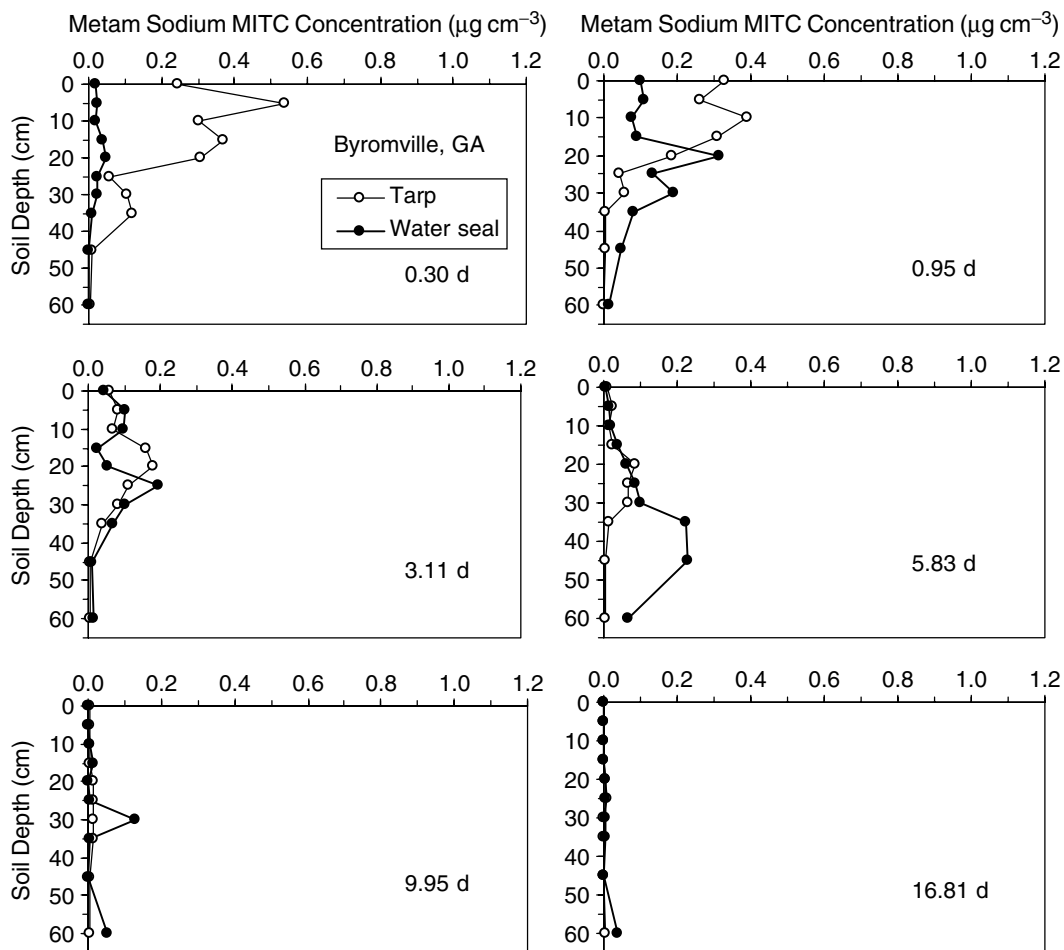
Relatively higher daily maximum wind speeds were observed at the Wisconsin nursery ( $\sim 6 \text{ m s}^{-1}$ ) than at the Georgia nursery ( $\sim 4 \text{ m s}^{-1}$ ) (Fig. 7). During the first 24 h after fumigation, daily maximum wind speeds were 6.2 and  $3.1 \text{ m s}^{-1}$  at the Wisconsin and Georgia nurseries respectively.

Air temperatures were generally lower at the Wisconsin nursery ( $5.0\text{--}28.3^\circ\text{C}$ ) than at the Georgia nursery ( $12.2\text{--}32.2^\circ\text{C}$ ) (Fig. 7). During the first 24 h after fumigation, air temperatures varied diurnally from  $7.8$  to  $21.7^\circ\text{C}$  at the Wisconsin nursery and from  $17.2$  to  $29.4^\circ\text{C}$  at the Georgia nursery. Differences

in air temperature would affect soil temperature and consequently the rate of fumigant diffusion in the soil.

At the Wisconsin nursery the clear plastic tarp cover increased soil temperatures at 10 cm depth by approximately  $10^\circ\text{C}$  compared with the water-sealed plots (Fig. 7). Because of lower latitude and higher air temperatures at the Georgia nursery, the increase in tarpred plots was only  $5^\circ\text{C}$ . Over the first 10 days the daily average soil temperature at the Wisconsin nursery decreased from  $28.8$  to  $24.5^\circ\text{C}$  in the tarpred plots and from  $23.4$  to  $20.6^\circ\text{C}$  in the water-sealed plots. At the Georgia nursery, average soil temperatures over the first 10 days remained about the same at  $30.2^\circ\text{C}$  in the tarpred plots but increased from  $24.8$  to  $25.6^\circ\text{C}$  in the water-sealed plots.

Because of differences in soil bulk density between the two experiment sites, volumetric soil moisture contents at 10 cm soil depth in the water-sealed plots were maintained at about  $0.25$  and  $0.20 \text{ cm}^3 \text{ cm}^{-3}$  during the first week of the Wisconsin and Georgia experiments respectively (Fig. 7). Moisture fluctuations during this time period were caused by responses to irrigation. After the last irrigation, soil moisture in the water-sealed plots started to decrease and reached  $0.22$  and  $0.15 \text{ cm}^3 \text{ cm}^{-3}$  by day 10 for the Wisconsin and Georgia nurseries respectively. The large spikes in moisture content on days 11 and 15 at the Wisconsin



**Figure 4.** Average concentrations of methyl isothiocyanate (MITC) in soil air at 0.30, 0.95, 3.11, 5.83, 9.95 and 16.81 days (d) after application of metam-sodium at Byromville, GA on 9 September 2003.

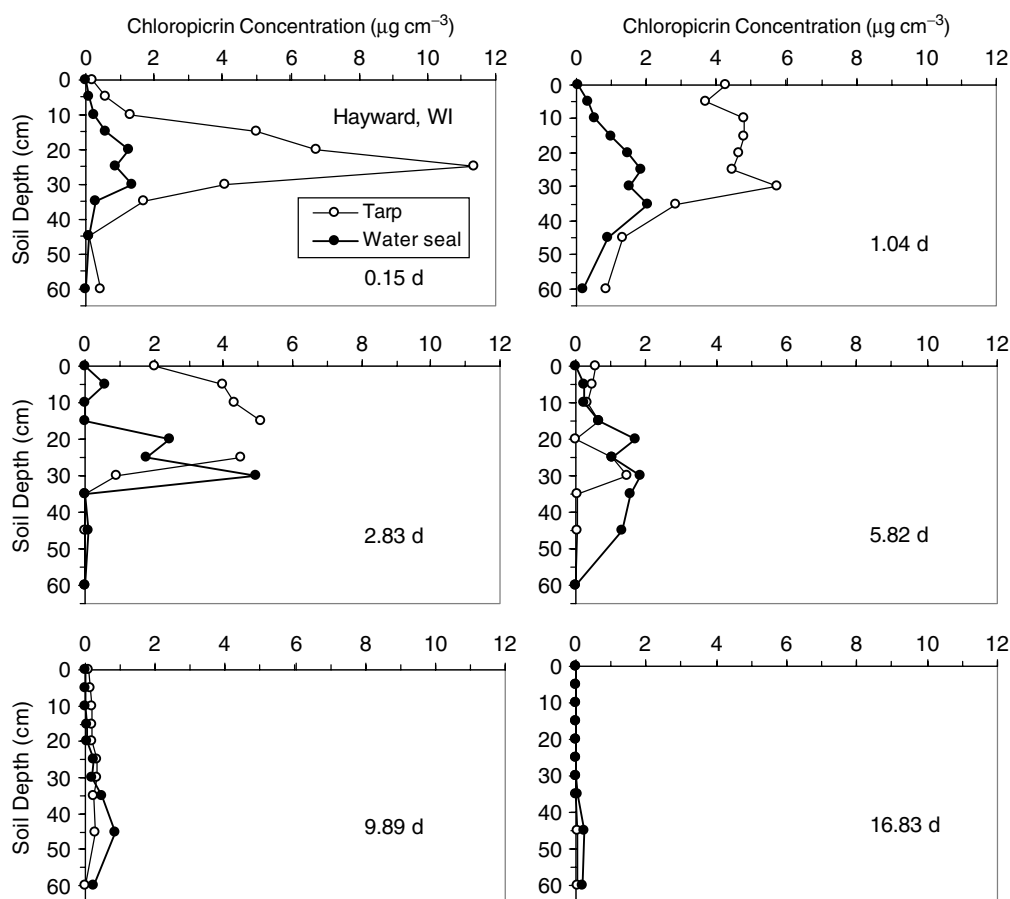
nursery and on day 14 at the Georgia nursery were the result of large rainfalls. Soil moisture in the tarped plots remained relatively constant during both experiments. Because of differences in soil bulk density, volumetric moisture contents in the tarped plots were about  $0.15$  and  $0.12 \text{ cm}^3 \text{ cm}^{-3}$  at the Wisconsin and Georgia nurseries respectively.

#### 4 DISCUSSION

A number of factors contributed to the MITC and CP distributions observed in these two nursery soils. The distribution of MITC and CP in soil varied greatly with the type of surface cover. Overall, the use of a plastic tarp cover greatly increased fumigant concentrations in the top 30 cm soil profile, but this effect lasted only about 3 days, after which most fumigants appeared to have been lost by soil degradation and volatilisation into the atmosphere. Conventional high-density polyethylene tarps are relatively permeable to MITC and CP gases,<sup>15</sup> and chemical dissipation is further dependent on environmental factors such as wind speed. Over bare soil (or water-sealed plots), greater wind speeds would accelerate fumigant dissipation from the soil by enhancing volatilisation losses into the atmosphere. The lower concentrations

of MITC and CP near the soil surface and their relatively faster dissipation at the Wisconsin nursery compared with the Georgia nursery were likely a result of the higher wind speed.

The extremely low dazomet MITC concentrations in the water-sealed plots at the Wisconsin nursery were mainly caused by irrigation on the first and second days after fumigant application. The total amount of water applied over the first 24 h following dazomet application was 53 mm. This large amount of water not only raised the soil moisture content significantly but also caused the fumigant to leach to lower depths. MITC concentrations were elevated at lower depths on days 3.00, 5.98 and 9.05, and this phenomenon has also been observed in laboratory column studies by other researchers.<sup>16–18</sup> The high moisture content also reduced soil effective porosity, which would slow fumigant diffusion at the Wisconsin nursery. For a bulk density of  $1.61 \text{ g cm}^{-3}$ , a moisture content of  $0.25 \text{ cm}^3 \text{ cm}^{-3}$  and assuming a particle density of  $2.65 \text{ g cm}^{-3}$ , the apparent soil porosity should have been 14%. In contrast to results at the Wisconsin nursery, significant levels of MITC were found in the upper 30 cm of soil in the water-sealed plots following dazomet application at the Georgia nursery. A total of 30 mm of water was applied over the first



**Figure 5.** Average concentrations of chloropicrin in soil air at 0.15, 1.04, 2.83, 5.82, 9.89 and 16.83 days (d) after injection at Hayward, WI on 6 August 2002.

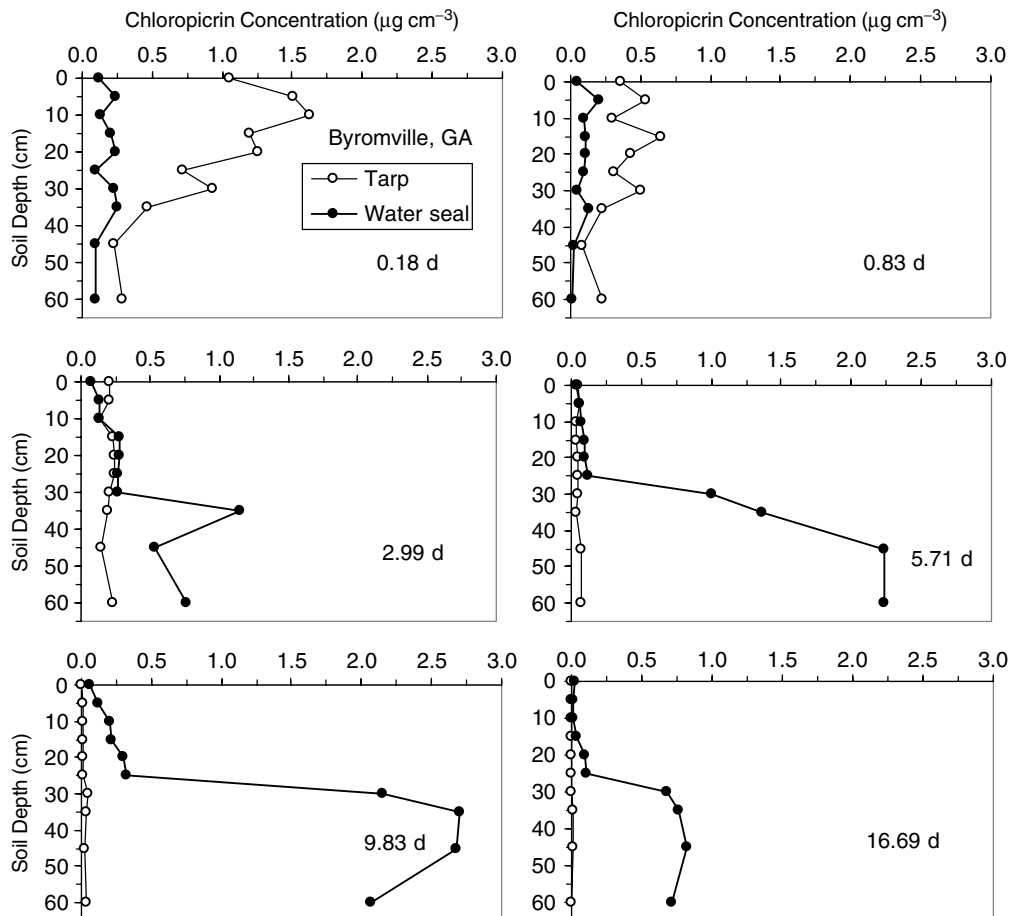
24 h following dazomet application. The relatively lower amount of water applied through irrigation and the lower soil bulk density at the Georgia nursery compared with the Wisconsin nursery may be the important factors affecting activation and distribution of MITC. For a bulk density of  $1.36 \text{ g cm}^{-3}$  and a moisture content of  $0.20 \text{ cm}^3 \text{ cm}^{-3}$  at the Georgia nursery the apparent soil porosity should have been 29%, more than double that at the Wisconsin nursery. The influence of soil moisture on fumigant distribution has been previously reported for other fumigant chemicals.<sup>19</sup>

Soil and environmental factors can also affect the rate of conversion from dazomet to MITC. Dazomet generally converts to MITC at an accelerated rate under higher moisture, higher temperature and higher pH conditions.<sup>20</sup> Soil moisture did not appear to be a limiting factor at either nursery, since MITC quickly reached maximum concentrations in the tarped plots where soil moisture was consistently lower than respective values in the water-sealed plots. The quick conversion to MITC in the tarped plots was likely attributable to elevated soil temperatures. Near the beginning of both experiments, daily average soil temperature at 10 cm depth was  $5.4^\circ \text{C}$  higher in the tarped than in the water-sealed plots. Although the conversion of dazomet to MITC is generally favoured by high soil pH, differences in soil pH between the two

nursery soils (i.e. 5.6 *vs* 6.8) would not significantly affect the conversion rate based on laboratory tests reported by Munnecke and Martin.<sup>20</sup>

The large amount of irrigation water also significantly reduced metam-sodium MITC concentrations in the water-sealed plots at the Wisconsin nursery compared with the Georgia nursery. Note that, in the Wisconsin experiment, metam-sodium was applied 1 day before dazomet, and the first sampling event (0.15 days) was made on the evening of the metam-sodium application before the site was irrigated with 25 mm of water on the following day. The overall MITC concentrations from metam-sodium in the water-sealed or tarped plots were relatively lower and dissipated faster at the Wisconsin than at the Georgia nursery. This was likely attributable to a faster rate of MITC degradation caused by a history of soil fumigation with MITC products at the Wisconsin nursery. MITC has been reported to degrade faster after repeated applications of metam-sodium<sup>21</sup> and, in a recent laboratory study, repeated metam-sodium or dazomet applications reduced MITC half-life to 5–30 h in a variety of soil types.<sup>22</sup> Similar MITC concentrations from dazomet in the tarped plots at the two nurseries would likely be attributable to faster conversion (from dazomet to MITC) and tarp entrapment, such that enhanced degradation, as a result of MITC history at the Wisconsin nursery, would not be





**Figure 6.** Average concentrations of chloropicrin in soil air at 0.18, 0.83, 2.99, 5.71, 9.83 and 16.69 days (d) after injection at Byromville, GA on 9 September 2003.

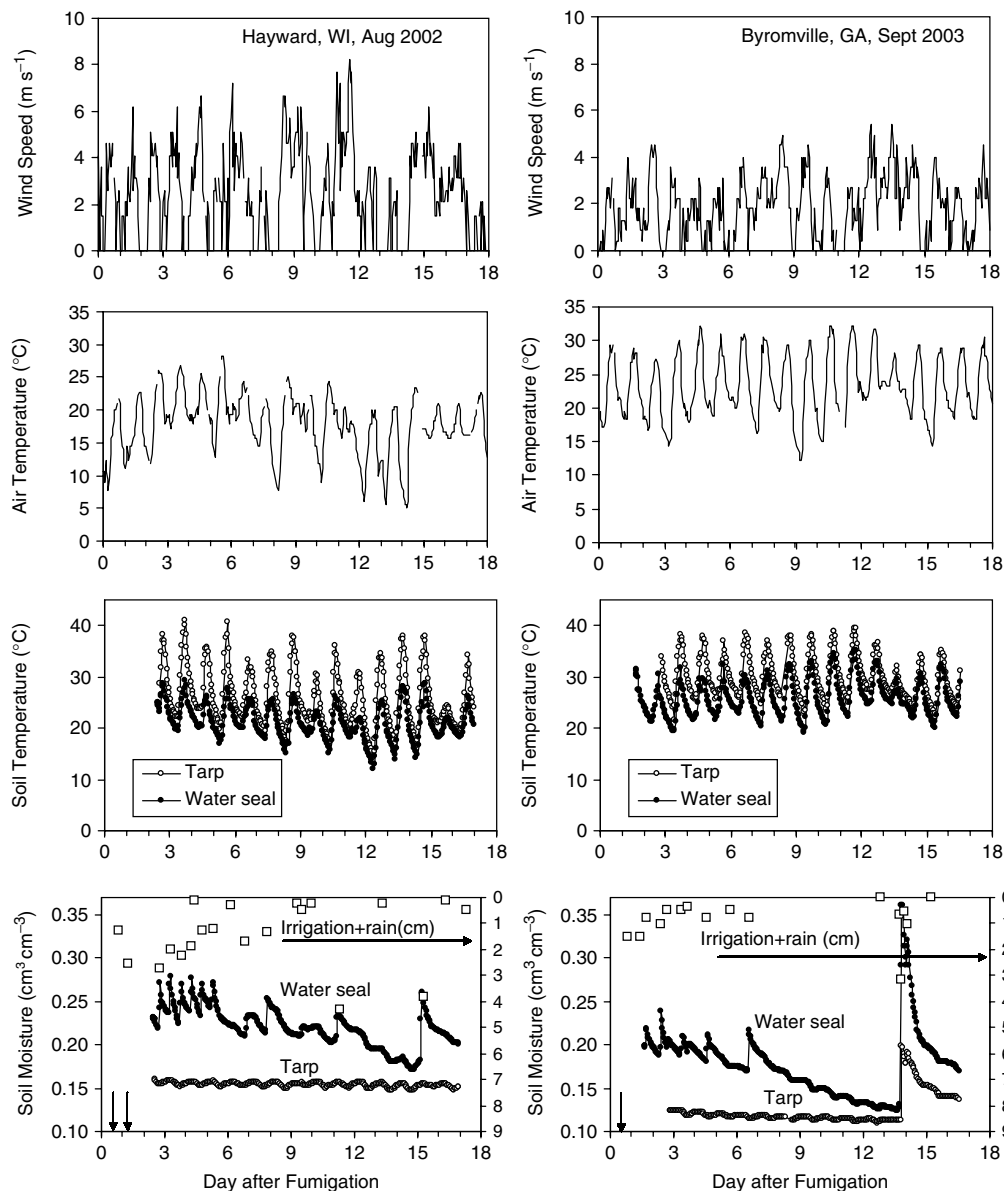
as apparent as in the water-sealed or metam-sodium plots.

Distributions of CP gases over time and soil depths followed a general trend that has been seen in another recent field study<sup>23</sup> and can generally be predicted by diffusion theory.<sup>24</sup> A peculiarity in CP distribution was the sustained high concentrations that occurred below 30 cm depth in the water-sealed plots at the Georgia but not the Wisconsin nursery. This phenomenon was most likely caused by the extremely low degradation rate of CP in water (half-life  $\sim 11$  years).<sup>25</sup> Whereas soil moisture content at 10 cm depth was about 0.25 and 0.20  $\text{cm}^3 \text{cm}^{-3}$  during the first week of the Wisconsin and Georgia experiments respectively, TDR measurements at 30 and 40 cm depths showed significantly higher moisture values at the Georgia than at the Wisconsin site for the entire duration ( $\sim 17$  days) of the experiments. At the Wisconsin nursery, average soil moisture decreased from 0.15  $\text{cm}^3 \text{cm}^{-3}$  during the first week to about 0.12  $\text{cm}^3 \text{cm}^{-3}$  at day 15. In contrast, soil moisture at the Georgia nursery remained almost constant at 0.20 and 0.17  $\text{cm}^3 \text{cm}^{-3}$  at 30 and 40 cm depths respectively. The high moisture content at the Georgia nursery was caused by a distinctively dense layer (plough pan) observed at about 40 cm depth where bulk density increased from 1.46 to 1.63  $\text{g cm}^{-3}$ . This dense layer literally created a nearly

impermeable barrier for water, causing water to collect and accumulate above this layer. The unexpected increase in moisture content in the tarped plots on day 14 at the Georgia nursery was due to a large rainfall followed by lateral water flow from outside the tarped areas. Except for a thin gravel layer at 30 cm, no distinctively dense layer was noted at the Wisconsin nursery.

## 5 CONCLUSIONS

Important selection criteria for determining effective methyl bromide alternatives to support seedling production in forest-tree nurseries include fumigant distribution and dissipation characteristics following application. In this study the spatial and temporal dynamics of MITC and CP in soil air from two forest-tree nurseries were measured following fumigation with dazomet, metam-sodium and CP under tarp and water seal covers. Significantly higher MITC and CP concentrations were typically observed under the tarp than the water seal covers. MITC and CP were concentrated in the upper 30 cm soil profile under tarp and the effect lasted for about 3 days. MITC concentrations in soil air were similar in dazomet or metam-sodium applications under tarp. The much lower fumigant concentrations in the



**Figure 7.** Wind speed, air temperature, soil temperature and soil moisture during the fumigation experiments at Hayward, WI and Byromville, GA. Day after fumigation was referenced to 12:00 on 6 August 2002 and 12:00 on 9 September 2003 for the Hayward and Byromville experiments respectively. The first arrow in the lower left graph points to the time (14:10 on 6 August) of metam-sodium and chloropicrin application and the second arrow to the time (10:45 on 7 August) of dazomet application at Hayward, WI. The arrow in the lower right graph indicates the time (11:30 on 9 September) of dazomet and metam-sodium application at Byromville, GA, where chloropicrin was injected 4 h later. Soil temperature and moisture data were for the 10 cm depth measurement from tarp and water seal treatments respectively. Open squares represent the sum of irrigation and rain (cm).

water-sealed plots, especially near the soil surface, would not likely provide sufficient exposure time in order to achieve desired pesticidal efficacy. Despite potential environmental and economic benefits with the water seal method, fumigant concentrations under the water seal cover were very sensitive to irrigation management, soil bulk density and other environmental conditions. As a result, fumigant gas distribution within the vertical soil profile was very unpredictable under the water seal cover.

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