From Forest Nursery Notes, Winter 2009

3. Methyl isothiocyanate and chloropicrin concentrations in bareroot forest nursery soils and above soil surface treatment following fumigation.
Juzwik, J. National Proceedings: Forest and Conservation Nursery Associations 2007, p. 38-45. USDA Forest Service, Rocky Mountain Research Station, Proceedings RMRS-P-57. 2008.

Methyl Isothiocyanate and Chloropicrin Concentrations in Bareroot Forest Nursery Soils and Above Soil Surface Treatment Following Fumigation

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Juzwik J. 2008. Methyl isothiocyanate and chloropicrin concentrations in bareroot forest nursery soils and above soil surface treatments following fumigation. In: Dumroese RK, Riley LE, technical coordinators. National Proceedings: Forest and Conservation Nursery Associations—2007. Fort Collins (CO): USDA Forest Service, Rocky Mountain Research Station. Proceedings RMRS-P-57:38-45. Available at: http://www.fs.fed.us/rm/pubs/rmrs_p057.html

ABSTRACT

Concentrations of methyl isothiocyanate (MITC) and chloropicrin (CP) in air spaces of nursery soil and in air at the soil surface following fumigation were determined in field trials in a Wisconsin and a Georgia nursery. MITC was measured in plots receiving either dazomet or co-application of metam sodium and chloropicrin; CP was measured in the latter plots. Soil surfaces were sealed with either a high density polyethylene tarp or by surface compaction and maintenance of a water seal following fumigation. Findings from the Wisconsin trial are highlighted. A very small percentage (< 3%) of the applied MITC was lost to the atmosphere, either through the plastic or water-sealed surfaces during the 14 days following treatment. For CP, 10% and 22% of the applied equivalent were calculated to have been lost to the atmosphere in the plastic-covered and water-sealed plots, respectively. Low MITC air emissions and MITC presence deep in the soil profile in the dazomet, water-sealed plots are partly attributed to over-irrigation on 5 of the 7 days following fumigation in Wisconsin. However, slightly higher, but still low, emissions in similar plots without excess watering in the Georgia nursery show that either surface containment method can be used in nurseries to reduce risk of MITC emissions to nearby seedling crops or harm to humans in nearby fields. The use of plastic tarps increases death rates of *Fusarium* propagules by maintaining higher chemical levels in the soil profile over time; however, dazomet has been used with water-seal treatment to give consistent, satisfactory control of soilborne pests in nurseries in the northern US.

KEYWORDS

dazomet, metam sodium, methyl bromide alternatives, soilborne pests, disease control

Introduction

The production of methyl bromide (MB) for routine soil fumigation is being phased out in anticipation of a full ban on its use for this purpose in the future. Recently, bareroot soils in some forest nurseries have been fumigated with MB by meeting the criteria for Critical Use Exemption and/or Quarantine and Pre-Shipment Uses. With the impending loss of MB, nurseries require economical, effective, and practical alternatives to the chemical in order to produce needed quantities of high quality tree seedlings.

Two promising chemical alternatives are dazomet for northern US nurseries (Borkenhagen 1994), and co-application of metam sodium and chloropicrin (CMS) for southern US nurseries (Carey 2000). Because methyl isothiocyanate (MITC) is the primary breakdown product from both chemicals, however, seedling damage and mortality in adjacent fields has been attributed to these alternative fumigants (Scholtes 1989; Carey 2000; Buzzo 2003). Collateral seedling damage was observed with CMS in an east Texas location when a temperature inversion occurred within 24 hours of the fumigation. The observed damage and subsequent attribution of the damage to "out-gassing" of MITC also raised concerns about possible toxicity to nursery workers in nearby fields. However, the surface containment methods associated with the reported "out-gassing" events appeared to be less than the minimum recommended for the products used based on available, published information. For example, manufacturer guidelines for dazomet fumigation state that the soil moisture at time of fumigation should be between 60% and 80% of maximum water-holding capacity. Immediately following fumigant incorporation, the soil surface is to be compacted with a roller and irrigation water applied daily during the first week in the amounts specified for Basamid® by Pennington (1995).

Amounts of MITC and CP that escape into the atmosphere after fumigation of forest nursery soils have not been published. Knowledge of gas movement through the soil profile to the surface is also lacking. Field studies were therefore initiated in a Wisconsin and a Georgia nursery by a team of soil scientists and plant pathologists to evaluate the potential for phytotoxicity and human toxicity in nearby fields following fumigation with either dazomet or CMS. The specific objectives were to measure: 1) soil gas concentrations and distribution patterns of MITC and CP; 2) emission flux and total emission loss of MITC and CP from treated nursery soil plots; and 3) levels of soilborne pathogens before and after treatment. Full results of these studies have been published in scientific journals (Wang and others 2005; Wang and others 2006) and readers are referred to these papers for in-depth findings. A synthesis and the author's interpretation of the key findings of these studies are presented in this paper. Although the focus is on results from the Wisconsin nursery, selected findings from the Georgia nursery are useful in the interpretation of the Wisconsin results.

Methods

Study Sites

Field studies were conducted in 2002 at the Hayward Nursery, Hayward, Wisconsin, and in 2003 at the Flint River Nursery, Byromville, Georgia. Soils in the fumigated fields at each nursery were loamy sands (average 86% and 88% sand in the upper 30.5 cm [12 in] of soil, Georgia and Wisconsin nurseries, respectively) with low organic carbon (< 1.1% and 1.4%, Georgia and Wisconsin, respectively).

Experimental Design

Four treatment combinations were used, including combinations of dazomet or co-application of chloropicrin and metam sodium, and 2 surface containment treatments (high density polyethylene tarps or surface compaction and maintenance of water seal per Pennington [1995]). A randomized complete block design with 4 replications was used in each of 2 field sections, that is, water-sealed versus plastic-sealed sections.

Chemical Treatment Specifications

Dazomet (Basamid®)

In Wisconsin, both 336 kg/ha (300 lb/ac) (incorporated with rotary tiller for maximum depth of incorporation at 13 to 15 cm [5 to 6 in]) and 448 kg/ha (400 lb/ac) (incorporated with a spading machine with maximum depth of incorporation at 20 to 23 cm [8 to 9 in]) rates of the product were applied. In Georgia, 560 kg/ha (500 lb/ac) product was applied and rototilled to a 20 cm (8 in) depth.

Metam Sodium (Vapam®)

In Georgia and Wisconsin, 700 l/ha (75 gal/ac) rate of metam sodium was sprayed on the soil surface and incorporated by tillers to the maximum depth possible (13 cm [5 in] in Wisconsin; 20 cm [8 in] in Georgia).

Chloropicrin (Chloro-O-Pic®)

The chloropicrin treatment occurred no later than 2 hours after application of the metam sodium. Shank injection of 112 kg/ha (100 lb/ac) of chloropicrin was done to a 20 to 25 cm (8 to 10 in) depth in both nurseries.

Sampling and Measurements

Rain gauges were installed inside and outside the water-sealed plots to measure water delivered via irrigation and rain at each location. Soil water content was measured in the plastic-covered and water-sealed plots at multiple depths using time domain reflectrometry (Wang and others 1998). Air and soil temperatures were measured in tarped and water-sealed plots using an automated thermocouple system (Wang and others 1998).

In both locations, atmospheric emissions of MITC and CP were measured with passive flux chambers modified from heavy-duty aluminum trays (25 x 48 x 15 cm [10 x 19 x 6 in]). To capture volatilized MITC and CP, air was drawn from the chambers through activated charcoal (for MITC) and polymer-based XAD tubes (for CP) at various times following fumigation.

Multiple port soil air sampling probes were used to sample MITC and CP concentrations at various depths in the soils of the treated plots. The probes were made with 127-cm (50-in) aluminum pipes fitted with 10 PTFE tubes. A 10-port air sampler was used to simultaneously withdraw air samples from each of the 10 tubes on the sampling probes.

Soil samples for fungal assay were taken from all plots the day before and 4 weeks after fumigation using a lined, tube sampler. Ten cores per plot were collected, each core sectioned sequentially into 5-cm (2-in) increments, and increment cores composited by depth for a plot.

Sample Analyses

Analyses of air emission and soil gas samples were made using a gas chromatograph with an electron capture detector and a nitrogen-phosphorous detector connected to a headspace auto-sampler. Separate capillary columns were used for MITC and CP. The amount of each chemical captured from each sample tube was quantified in the capture detector. Calibration standards were routinely run for each chemical. Collected soil samples were assayed for *Fusarium* spp. using the technique of soil dilution plating onto selective media in Petri dishes (Juzwik and others 1999).

Results

Chemical Levels in Soil Air

The highest concentrations of all 3 chemicals in the top 20 to 36 cm (8 to 14 in) of soil occurred during the first 3 days after soil fumigation in the plots with plastic-sealed surfaces (Table 1). In the rolled and water-sealed field section, peak concentrations of MITC from dazomet were found at a greater soil depth (20 to 51 cm [8 to 20 in]) than the depths for the peak MITC levels in the CMS plots (0 to 36 cm [0 to 14 in]). The time periods during which peak chemical concentrations were found were quite variable with the longer time periods associated with the metam sodium+ chloropicrin treatment in the water-sealed plots.

Table 1. Summary of methyl isothiocyanate (MITC) or chloropicrin (CP) detected at various depths below soil surface and over time (days) in plots receiving fumigation x soil surface treatments in the Wisconsin nursery.

Treatment combination[z]	Maximum Chemical Concentrations Detected			
	Chemical measured	Soil depth (in)	Amount (mg/m^3)	Time period (after fumigation)
Dazomet/spade/plastic	MITC	2 to 8	150 to 550	2 hr to 3 days
Dazomet/spade/water	MITC	8 to 18	50 to 300	6 hr to 6 days
Dazomet/rotary tiller/water	MITC	8 to 20	50 to 150	6 hr to 3 days
Metam sodium/rotarty tiller/plastic	MITC	2 to 12	120 to 420	< 30 hr
Chloropicrin/rotary tiller/plastic	CP	0 to 14	1500 to 11,500	< 30 hr
Metam sodium/rotary tiller/water	MITC	0 to 14	50 to 350	6 hr to 7 days
Chloropicrin/rotary tiller/water	CP	4 to 14	1000 to 5000	3 hr to 7 days

[z] See methods section for full description of treatments
1 in = 2.5 cm

Chemical Levels in Atmospheric Emissions

The highest level of MITC emissions to the atmosphere (as measured by flux, that is, $\mu g/m^2$/second) occurred in the CMS plots (Table 2). These peak emissions occurred over a longer time period for the plastic-covered plots compared to the water-sealed plots. The maximum CP flux to the atmosphere occurred between day 1 and day 4 after fumigation, regardless of surface treatment. CP flux was highest in the water-sealed plots. MITC emissions from dazomet/water-sealed plots were very low (Table 2).

A very small percentage (< 3%) of the applied equivalent of MITC was lost to the atmosphere, either through the plastic or water-sealed surface, during the 2-week period following soil fumigation. For CP, 10% and 22% of the applied equivalent were calculated to have been lost to the atmosphere in the plastic-covered and the water-sealed plots, respectively.

Fusarium spp. Occurrence in Soil

Prior to soil fumigation, *Fusarium* spp. were commonly present in the 4 replicate soil samples of all study plots in the upper 21.5 cm (8.5 in) of soil (Table 3). Lower incidences of *Fusarium* spp. occurrence were found in soil from lower depths (between 21.5 and 42 cm [8.5 and 16.5 in]). *Fusarium* spp. levels in post-treatment samples from the top 21.5 cm (8.5 in) in the soil profile differed by treatment combination. Fungal occurrence was lowest and similar in the dazomet and the metam sodium+chloropicrin plots where plastic covered the soil surface ($P < 0.02$). Little reduction in *Fusarium* spp. occurrence between pre- and post-treatment samples was found for the dazomet/rototilled/water-sealed and the metam sodium+chloropicrin/rototilled/water-sealed plots.

Irrigation and Rain Water Levels

The amount of irrigation water delivered to the water-sealed plots daily exceeded the intended target amount on days 2 through 7 following soil

Table 2. Summary of emission flux of methyl isothiocyanate (MITC) and chloropicrin (CP) over time through 2 surface treatments following soil fumigation with dazomet and co-applied metam sodium+chloropicrin in the Wisconsin nursery.

Treatment combination[z]	Chemical measured	Maximum chemical emission Flux rate ($\mu g/m^2/sec$)	Time period (after fumigation)
Dazomet/spade/plastic	MITC	1 to 3	1 to 5 days
Dazomet/spade/water	MITC	< 1	2 days
Dazomet/rotary tiller/water	MITC	negligible	6 hr to 3 days
Metam sodium/rotary tiller/plastic	MITC	2.5 to 25	1 to 3 days
Chloropicrin/rotary tiller/plastic	CP	5 to 15	1 to 4 days
Metam sodium/rotary tiller/water	MITC	< 2.5	1 to 2 days
Chloropicrin/rotary tiller/water	CP	4 to 64	1 to 4 days

[a] See methods section for full description of treatments

Table 3. Incidences of *Fusarium* spp. isolation from replicate soil samples by soil depth and treatment before and after soil fumigation in the Wisconsin nursery.

Soil Depth (inches)	Pre-fumigation assay by treatment[z]					Post-fumigation assay by treatment				
	D/SP/W	D/SP/P	D/RT/W	CMS/RT/W	CMS/RT/P	D/SP/W	D/SP/P	D/RT/W	CMS/RT/W	MSC/RT/P
0 to 3	++++[y]	++++	+++ -	++++	++++	+++ -	- - - -	++++	++++	++ - -
3 to 5.5	+++ -	++++	++++	++++	++++	++ - -	++ - -	++++	++++	- - - -
5.5 to 8.5	++++	++++	++++	++++	+++ -	+ - - -	+ - - -	++++	++ - -	- - - -
8.5 to 11	++ - -	+++ -	- - - -	+ - - -	+ - - -	+ - - -	+ - - -	+ - - -	+ - - -	- - - -
11 to 14	+ - - -	- - - -	+ - - -	+ - - -	- - - -	- - - -	- - - -	- - - -	+ - - -	- - - -
14 to 16.5	+ - - -	+ - - -	++ - -	++ - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -

[z] Treatment descriptions: D/SP/W = dazomet/spade/water-seal; D/SP/P = dazomet/spade/plastic-seal; D/RT/W = dazomet/rotary tilled/water-seal; CMS/RT/W = chloropicrin/rotary tilled/water-seal; CMS/RT/P = chloropicrin/rotary tilled/plastic-seal. See methods section for futher details.
[y] + = *Fusarium* spp. isolated; - = no *Fusarium* spp. isolated from a replicate soil sample.
1 in = 2.5 cm

fumigation (Table 4). Negligible rainfall was received on 2 of the first 7 days following fumigation.

Discussion

With both surface treatments used in the Wisconsin and Georgia studies, more than 70% of total cumulative emissions of either MITC or CP occurred within 1 week of fumigant application. The final cumulative MITC emission losses accounted for a very small percentage of the equivalent MITC applied as either dazomet or metam sodium. This may be partly due to accelerated rates of MITC degradation in the soil. The short duration and the negligible levels of MITC emission from water-sealed plots is likely due, in part, to accelerated transformation of product to MITC in the first case and percolation of product to greater depths resulting in lower emissions in the second case. The excessive irrigation in the water-sealed plots in the Wisconsin nursery, thus, must be considered in the interpretation of the air emissions results. The fungal presence data suggests that concentrations of MITC in the upper 21.5 cm (8.5 in) of soil in the water-sealed plots were not sufficient to kill most *Fusarium* propagules. In addition, the recorded emissions of MITC in the Georgia nursery study are helpful in interpreting the Wisconsin MITC emissions results. Specifically, the percentages of applied equivalent of MITC lost to the atmosphere in dazomet/water-sealed plots in Wisconsin were one-tenth that of emissions in similar plots in the Georgia nursery (Table 5), supporting the interpretation that excess irrigation water was partly responsible for the very low emissions. Regardless of the irrigation water issue in the Wisconsin study, the very small percentage of MITC lost to the atmosphere through either surface treatment is not likely to result in damage to crops in adjacent fields and is much below the level known to

Table 4. Amount of irrigation and rain water measured in treatment plots during the 7 days following soil fumigation in the Wisconsin nursery.

Number of days after fumigation	Amount (in) of Irrigation Water		Amount (in) of Rain Water
	Targeted[z]	Actual	
0	3/4 to 1	1/2	0
1	1/2 + 1/2[y]	1	0
2	1/4 + 1/4	1	0
3	1/8 + 1/8	1 2/3	0
4	1/8 + 1/8	1 1/3	0
5	1/8 + 1/8	1/2	< 1/10
6	0	4/5 + 1	0
7	0	2/3 + 1/2	< 1/10

[z] Based on recommended irrigation schedule for Basamid¤ as outlined in Pennington (1995).

[y] Indicates split irrigation (morning plus afternoon)

1 in = 2.5 cm

Table 5. Comparison of cumulative emission losses of methyl isothiocyanate following dazomet fumigation in water-sealed plots at the Wisconsin and Georgia nurseries.

Nursery Location	Treatment [z]	Final Cumulative Emission mg/m²	as percentage [y]
Wisconsin	Dazomet / spading machine	48	0.3
Wisconsin	Dazomet / rotary tiller	8	0.1
Georgia	Dazomet / rotary tiller	727	3.2

[z] 450 kg/ac (400 lb/ac) dazomet incorporated to 20 to 23 cm (8 to 9 in) depth using a spading machine; 336 kg/ha (300 lb/ac) dazomet incorporated to 13 to 15 cm (5 to 6 in) depth using a rotary tiller; 560 kg/ha (500 lb/ac) dazomet incorporated to 20 cm (8 in) depth using a rotary tiller.

[y] Assumed on a molar basis 100% conversion from dazomet to metam sodium (Kim and others 1994).

be a lethal threat to humans near fumigated fields (Wang and others 2005).

Implications for Nursery Managers

Use of surface compaction plus a water seal or plastic tarps delays and/or reduces the emission of MITC to the atmosphere compared to situations where no water-seal or plastic is used when fumigating with MITC-generating products. Thus, 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.

The use of either surface containment method in operational fumigation would also increase the concentration, over time, of MITC in the soil and result in reduced populations of soilborne pests. Careful attention, however, must be paid to irrigation water amounts used to maintain water seals for dazomet fumigation. Too much water can result in little to no efficacy in reducing fungal populations in the soil. Logically speaking, plastic tarp use eliminates concerns about excess irrigation water or significant rainfall events and would maintain the chemical concentration over a sufficient period of time to significantly reduce levels of soilborne pests. With careful oversight and planning, however, MITC generating products can be applied in such a manner to give consistent and satisfactory control for soilborne pests in nurseries in the northern US (Borkenhagen 1994; Juzwik and others 2002).

Acknowledgments

The studies discussed in this paper were conducted as a joint effort of the following individuals and the author: Dong Wang, Research Leader, USDA Agricultural Research Service (ARS), Parlier, California; K Spokas, Research Soil Scientist, USDA ARS, St Paul, Minnesota; Y Zhang, Postdoctoral Scientist, Department of Soil, Water, and Climate, University of Minnesota, St Paul; Stephen Fraedrich, Research Plant Pathologist, USDA Forest Service, Southern Research Station, Athens, Georgia; and William Koskinen, USDA ARS, St Paul, Minnesota. The author thanks

Gordy Christians and staff at the Hayward State Nursery and Jeff Fields, Greg Seabolt, and staff at the Flint River State Nursery for providing study sites and technical assistance. Susan Best, Tony Blalock, Kathy Kromroy, and Matt Ruark provided excellent field assistance. The metam sodium application in Wisconsin and chloropicrin application in both locations were generously provided by Steve Godbehere, Hendrix and Dail. Majority of the funding for this project was from the USDA Cooperative State Research, Education, and Extension Service (CSREES) Methyl Bromide Transitions Program.

References

Borkenhagen JE. 1994. Basamid use and results in the Hayward State Nursery. In: Landis TD, Dumroese RK, technical coordinators. National proceedings: forest and conservation nursery associations. Ft Collins (CO): USDA Forest Service, Rocky Mountain Research Station. General Technical Report RM-GTR-257. p 16-18.

Buzzo RJ. 2003. Phytotoxicity with metam sodium. In: Riley LE, Dumroese RK, Landis TD, technical coordinators. National proceedings: forest and conservation nursery associations—2002. Ogden (UT): USDA Forest Service, Rocky Mountain Research Station. Proceedings RMRS-P-28. p 79-83.

Carey WA. 2000. Producing southern pine seedlings with methyl bromide alternatives. In: Proceedings of the 2000 international research conference on methyl bromide alternatives and emission reductions; 2000 November 6-9; Orlando, FL. Fresno (CA): Methyl Bromide Alternatives Outreach. Paper 51. p 1-3.

Juzwik J, Gust KM, Allmaras RR. 1999. Influence of cultural practices on edaphic factors related to root disease in *Pinus* nursery seedlings. Plant and Soil 207:195-208.

Juzwik J, Kromroy KW, Allmaras RR. 2002. Comparison of tillage equipment for improving soil conditions and root health in bareroot nurseries. In: Dumroese RK, Riley LE, Landis TD, technical coordinators. National proceedings: forest and conservation nursery associations—1999, 2000, and 2001. Ogden (UT): USDA Forest Service, Rocky Mountain Research Station. Proceedings RMRS-P-24. p 103-111.

Kim JH, Lam WW, Quistad GB, Casida JE. 1994. Sulfoxidation of the soil fumigants metam sodium, methyl isothiocyanate, and dazomet. Journal of Agriculture and Food Chemistry 42:2019-2024.

Pennington W. 1995. Basamid granule soil fumigant: preplant soil fumigation update. In: Landis TD, Cregg B, editors. National proceedings: forest and conservation nursery associations. Portland (OR): USDA Forest Service, Pacific Northwest Research Station. General Technical Report PNW-GTR-365. p 13-14.

Scholtes JR. 1989. Soil fumigation at J. Herbert Stone Nursery. In: Landis TD, technical coordinator. Proceedings, Intermountain Forest Nursery Association; 1989 Aug 14-17; Bismarck, ND. Fort Collins (CO): USDA Forest Service, Rocky Mountain Research Station. General Technical Report RM-184. p 35-37.

Wang D, Yates SR, Ernst FF. 1998. Determining soil hydraulic properties using tension infiltrometers, TDR, and tensiometers. Soil Science Society of America Journal 62:318-325.

Wang D, Juzwik J, Fraedrich SW, Spokas K, Zhang Y, Koskinen WC. 2005. Atmospheric emissions of methyl isothiocyanate and chloropicrin following soil fumigation and surface containment treatment in bare-root forest nurseries. Canadian Journal of Forest Research 35:1202-1212.

Wang D, Fraedrich SW, Juzwik J, Spokas K, Zhang Y, Koskinen WC. 2006. Fumigant concentration distribution in forest nursery soils under water seal and plastic film after application of dazomet, metam sodium, and chloropicrin. Pest Management Science 62:263-273.