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Degradation of Methyl Isothiocyanate and Chloropicrin in Forest Nursery Soils

Y. Zhang,* K. Spokas, and D. Wang

ABSTRACT

Recent studies have observed enhanced degradation of methyl isothiocyanate (MITC) from repeated fumigation in agricultural soils. Little is known about fumigant degradation in forest and nursery soils. This study was conducted to determine degradation rates of MITC and chloropicrin (CP) in two forest soils and the impacts of nursery management on degradation of MITC and CP. The half-life values of MITC and CP were evaluated in the laboratory under isothermal conditions (22 ± 2°C). Three rates representing 0.5×, 1×, and 2× field application rates for each fumigant were used in laboratory incubations. Effect of microbial degradation was determined by conducting incubations with both fresh and sterilized soils. Soil moisture effects were also studied. There was no difference in MITC or CP degradation between fumigated and nonfumigated forest nursery soils. Soil sterilization and high soil moisture content (15% by wt.) reduced MITC and CP degradation. The degradation rates of MITC and CP varied with factors such as nursery history, fumigant application rates, and freshness of tested soils.

Soil fumigation is used to control soil-borne pathogens, parasitic nematodes, and weeds (United Nations Environmental Programmes, 1995). More than 68 000 ha of soil in the United States and more than 250 000 ha in the world were fumigated annually with methyl bromide (MeBr) (USDA, 2002). Production of tree seedlings in forest nurseries has relied on soil fumigation with MeBr for decades (Smith and Fraedrich, 1993). Serious environmental concern has been placed on several fumigants due to their high toxicity, carcinogenicity, or damage to stratospheric ozone (United Nations Environmental Programmes, 1995; Yagi et al., 1995). Methyl bromide is scheduled to be phased out in 2005 in the United States because of its effect on ozone depletion (Wofsy et al., 1975; Butler, 1995).

Several registered fumigants are intensively tested as alternatives to MeBr for their efficacy to control soil pests and environmental fate. Metam-sodium (sodium-*N*-methyl dithiocarbamate, $C_2H_4NS_2Na$) and dazomet (tetrahydro-3,5-dimethyl-2*H*-1,3,5-thiadiazine-2-thione, $C_5H_{10}N_2S_2$) are potential alternative soil fumigants to MeBr. Both compounds degrade into the active ingredient methyl isothiocyanate (MITC) that is responsible for pest control in soils (Saeed et al., 1997; Frick et al., 1998). Transformation and dissipation rates of MITC in agricultural soils are described by first-order degradation kinetics (Smelt and Leistra, 1974; Gerstl et al., 1977; Boesten et al., 1991; Warton et al., 2001; Dungan and Yates, 2003).

Chloropicrin (trichloronitromethane, CP) has been used for decades in soil fumigation together with MeBr as a warning agent due to its strong lachrymatory feature, or to achieve broad-spectrum control (Moldenke and Thies, 1996). In 1998, a total of 1.4 million kg of CP was used in California alone (California Department of Pesticide Regulation, 1999). Chloropicrin used in combination with a MITC generator can be as effective as MeBr in soil fumigation (Moldenke and Thies, 1996; South et al., 1997; Freitas et al., 1999; Trout and Ajwa, 1999; Carey, 2000). Chloropicrin can be dehalogenated by *Pseudomonas* spp., with the major metabolic pathway occurring through three successive reductive dehalogenations to nitromethane (Castro et al., 1983). Chloropicrin degraded very fast with a half-life ($t_{1/2}$) of only 1.3 h in an alfalfa-amended anaerobic soil (Wilhelm et al., 1997).

Reduced effectiveness of pest control from MITC has been observed in agricultural soils with repeated application (Smelt et al., 1989; Verhagen et al., 1996; Chung et al., 1999; Dungan and Yates, 2003; Di Primo et al., 2003). One explanation for the lowered pest control is the enhanced biodegradation of MITC due to soil enrichment of adapted MITC-degrading microbial populations (Roberts and Stoydin, 1976; Mulder, 1995; Di Primo et al., 2003; Dungan and Yates, 2003). The biological degradation could be enhanced by promoting the growth or stimulating the activity of fumigant-degrading microorganisms. The abiotic degradation of fumigants (e.g., CP and 1,3-D) could be accelerated by increasing the concentration of nucleophiles in soil (Gan et al., 1998; Dungan et al., 2001, 2003) and is affected by soil water content (Helweg, 1987; Choi et al., 1988; Walker et al., 1986; Gan et al., 1999). Accelerated transformation mechanism of CP and MITC was related to addition of compost or manure because more organic matter in soils can develop new microbial population with enhanced degradation capacity for MITC and CP (Ibekwe et al., 2001; Dungan et al., 2003). Physical and chemical properties such as texture, organic matter, and pH of soil can dramatically affect and further complicate the degradation of fumigants (Verhagen et al., 1996). Enhanced degradation of MITC occurred in soils after very intensive fumigation (six consecutive treatments in 1 yr), but the enhancement only lasted a limited period of time (2–3 yr) after field fumigation had ceased (Verhagen et al., 1996). However, little is known about degradation of MITC and CP in frequently fumigated nursery soils.

The objective of this study was to evaluate the degra-

Y. Zhang and D. Wang, Department of Soil, Water, and Climate, University of Minnesota, St. Paul, MN 55108. K. Spokas, USDA-ARS, North Central Soil Conservation Research Lab, Morris, MN 56267. Received 5 Oct. 2004. *Corresponding author (zhang251@umn.edu).

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677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: CP, chloropicrin; MITC, methyl isothiocyanate.

dation rates of MITC and CP in two nursery soils with fumigation history and in two forest soils without fumigation history.

MATERIALS AND METHODS

Soils

Four soils were used to ensure a variety of soil textures, fumigation histories, management, and geographical diversities. Two nursery soils with different fumigation histories were collected from the Hayward State Nursery (Hayward, Wisconsin) and the Flint River State Nursery (Byromville, Georgia) to represent two types of geographical conditions. Both nurseries have routinely fumigated soil to support bare-root seedling production. Information is listed on fumigation history of the nursery soils and estimated fumigants applied, to assess any impact that past fumigation may have on MITC and CP degradation (Table 1). Two forest soils without fumigation history were also collected in proximity of the two nurseries. Fumigant degradation in the forest soils without impact of nursery management was compared to those in the soils impacted by repeated fumigation. The conditions of sampling sites are summarized in Table 1.

Soil samples were collected from 0- to 15-cm depth with a 5-cm-diameter auger. Fresh soil was passed through a 2-mm sieve and stored at room temperature (22 ± 2°C). Incubation experiments were performed within four weeks after collection. The incubation of sterilized soils was conducted after finishing incubation tests of field-moist soils. Soil pH, moisture content, fractions of sand, silt, clay, and total organic carbon (TOC) were measured (Table 2). Soil water content was determined by oven-drying 10-g subsamples at 105°C for 24 h. Soil pH was measured in a 1:1 (v/v) slurry of soil and deionized water using a Hanna Instruments (Woonsocket, RI) portable pH/EC/TDS/temperature probe. Soil texture and TOC were determined with the hydrometer method (Gee and Bauder, 1986) and the loss on ignition method (Nelson and Sommers, 1996) by the University of Minnesota Soil and Plant Testing Laboratory.

Incubation Experiments

Triplicate incubations of each soil were performed to measure degradation rates following procedures modified from previous studies (Gan et al., 2000; Ma et al., 2001). Briefly, five grams (dry wt.) of fresh soil was weighed into 21-mL glass vials (Kimble Glass, Vineland, NJ). Standard MITC solutions were spiked in samples to create three dosages of 39.6, 79.3, and 158.5 mg kg^{-1} equivalent to a MITC field application rate of 195, 390, and 785 kg ha^{-1}, respectively, assuming a uniform distribution in the top 30 cm of soil with bulk density of 1.65 g cm^{-3}. These rates correspond to approximately 0.5×, 1×, and 2× the recommended field application rates for each chemical, respectively. Vials were capped immediately with aluminum seals and Teflon-faced butyl rubber septa (Agilent Technologies, Palo Alto, CA) and then incubated in the dark at room temperature (22 ± 2°C). Technical standards of MITC (99.5%) were purchased from Chem Service (West Chester, PA). The standard solutions of chemicals were prepared in deionized water immediately before use to prevent hydrolysis.

Triplicate vials were removed at seven elapsed times of 0, 4, 9, 24, 48, 96, and 168 h in incubation, and kept frozen at −20°C until gas chromatography (GC) analysis. For extraction, each of these vials was decapped, 5 g of anhydrous sodium sulfate and 5 mL of ethyl acetate were added, and the vial was immediately recapped. After soils were thawed for 20 min at room temperature, the vials were placed on a reciprocating shaker (Eberbach Corp., Ann Arbor, MI) for 1 h at high speed (approximately 150 min^{-1}). An aliquot of the supernatant from each vial was transferred into a GC vial for MITC analysis. Preliminary experiments indicated that recovery efficiency ranged from 89 to 105% using the above procedure.

The procedures for CP degradation experiments were similar to those for MITC except that the thawing time for vials was 15 min, and vials were shaken for 10 min for extraction before analysis. Chloropicrin was spiked into soils at three dosages of 28.3, 56.6, and 113.2 mg kg^{-1} for each soil, equivalent to the field application rates of 140, 280, and 560 kg ha^{-1} of CP, assuming CP applied uniformly in the top 30 cm of soil with bulk density of 1.65 g cm^{-3}.

To determine whether microbial or abiotic processes contributed to MITC and CP degradation, incubations were also performed with sterilized soils. Soils were sterilized by autoclaving three times at 121°C for 30 min with a 24-h interval. Sterilized deionized water was then added into the sterilized soil samples to bring soil water content back to its corresponding field-moist level as indicated in Table 2. Sterilized samples were spiked with fumigants at the same rates as for the fresh soils. All vials were incubated in the dark, and then triplicate samples were removed, extracted, and analyzed. The two fumigated nursery soils were sterilized for this evaluation.

To determine the effect of soil moisture on MITC and CP degradation, different amounts of deionized water were added to 5 g air-dried Hayward nursery soil to achieve four levels of final moisture levels: 0.5, 5, 10, and 15% (w/w). The fumigants were then spiked with 79.3 mg MITC kg^{-1} and 56.6 mg CP kg^{-1}, equivalent to the recommended field application rates of 390 kg ha^{-1} for MITC and 280 kg ha^{-1} of CP.

Table 1. Site characteristics.

Soil	Soil description	Fumigation history†	Soil management
	Hayward, Wisconsin (46.0° N, 91.3° W) site		
Nursery	Vilas loamy sand (sandy, mixed, frigid, Entic Haplorthod)	MeBr, CP, MITC; last fumigation was 2+ years ago	nursery for bare-root seedling production
Forest	same as above	none	forest
	Byromville, Georgia (32.2° N, 84.0° W) site		
Nursery	Eustis loamy sand (siliceous, thermic Psammentic Paleudult)	MeBr, CP; last fumigation was 2+ years ago	nursery for bare-root seedling production
Forest	same as above	none	forest

† MeBr, methyl bromide; MITC, methyl isothiocyanate; CP, chloropicrin. Fumigants used in nursery are listed in the order of application frequency and amount.

Table 2. Physical and chemical properties of soils used in incubation studies.†

Soil	pH	θ_w	Sand	Silt	Clay	TOC
		%				
		Hayward, Wisconsin site				
Nursery	6.8	5.02 ± 0.2	83.7	9.0	7.3	1.12 ± 0.01
Forest	5.8	1.46 ± 0.1	82.5	8.0	9.5	0.65 ± 0.03
		Byromville, Georgia site				
Nursery	5.6	7.0 ± 0.1	86.2	7.3	6.5	1.86 ± 0.01
Forest	5.9	4.6 ± 0.1	87.5	6.8	5.8	1.37 ± 0.01

† θ_w, soil moisture content by weight; TOC, total organic carbon. Data for θ_w and TOC are shown as the arithmetic means ± standard deviation (n = 3). Standard deviation is not shown for pH, sand, silt, or clay fractions.

Gas Chromatography Analysis

Analysis of MITC and CP concentrations was performed by an HP 5890A GC (Agilent Technologies) coupled with an HP-7694 headspace sampler (Agilent Technologies). Methyl isothiocyanate was determined with a nitrogen–phosphorus detector (NPD) and CP by an electron capture detector (ECD). They were quantified through a four-point external calibration within expected ranges. The detector temperatures for NPD and ECD were 220 and 250°C, respectively. A 30-m × 0.53-mm × 5-μm RTX-5 capillary column (Restek Corp., Bellefonte, PA) 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}. The oven temperature was held at 70°C for 7 min for both fumigants.

Statistical Analysis

The residual concentrations obtained at seven time points for each soil were fitted to a first-order kinetics model to compute the degradation rate constants k (d^{-1}) and half-life ($t_{1/2}$) values. Tukey's Honestly Significant Difference (HSD) tests were performed using STATISTICA 6.0 (StatSoft, 2002) to determine whether differences in fumigant degradation between selected variables were significant at $P < 0.05$.

RESULTS AND DISCUSSION

Effects of Nursery Location and Fumigation History

Methyl isothiocyanate and CP degradation followed a first-order kinetics in four soils ($r^2 = 0.85$–0.97, Fig. 1). Degradation rates of two fumigants varied considerably in nursery and forest soils (Table 3). Half-life ($t_{1/2}$) varied from 3.5 to 11.9 d for MITC and from 0.8 to 4.5 d for CP in two fumigated nursery soils, and from 3.1 to 11.2 d for MITC and from 0.8 to 5.5 d for CP in the two nonfumigated forest soils (Table 3). This agrees with previous studies on degradation rates in agricultural soils for MITC (Smelt and Leistra, 1974; Gerstl et al., 1977; Smelt et al., 1989; Boesten et al., 1991; Gan et al., 1998; Dungan et al., 2003) and for CP (Wilhelm et al., 1997; Gan et al., 2000). However, the $t_{1/2}$ values of two fumigants in our experiments showed a larger variation in triplicate samples than those published results of agricultural soils which were processed with air-drying, grinding, and freezing storage before incubation. In this study the fresh soils were used in incubation shortly after collection to reduce the effects of soil preparation procedures such as cold storage on the populations and activities of soil microbes (e.g., Stenberg et al., 1998).

For most treatments, no significant difference in $t_{1/2}$ was found between the fumigated nursery and nonfumigated forest soils for either MITC or CP (Table 3; Fig. 1). A faster degradation of MITC and CP was found only at application rates of 390 kg ha^{-1} MITC and 280 kg ha^{-1} CP in nursery soil (Wisconsin) than in the corresponding forest soil.

The response of MITC and CP degradation to change in application rate and soil type varied considerably in this experiment (Table 3). Generally there was no significant difference of either MITC or CP degradation between three application rates in both nursery and forest soils from Wisconsin and Georgia at $P < 0.05$ (Table 3). No correlation was found between application rate level and degradation rate of MITC and CP. A general trend was observed in an agricultural soil (Arlington sandy loam) that the degradation rate constant of MITC decreased with increasing initial concentration although such a trend is contradictory to the basic assumptions of first-order kinetics (Ma et al., 2001). However, the rea-

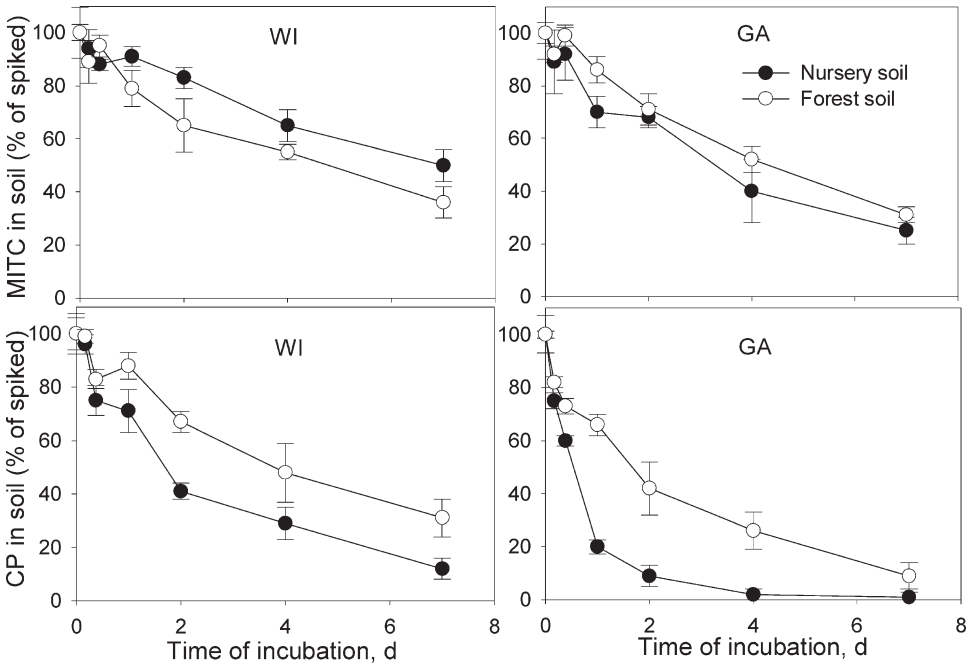

Fig. 1. Comparison of degradation of methyl isothiocyanate (MITC) and chloropicrin (CP) in two fumigated nursery soils and two nonfumigated forest soils at application rates of 195 kg ha^{-1} for MITC and 140 kg ha^{-1} for CP in incubation at 22°C. The points are means of triplicate samples (±standard errors).

son for this discrepancy between this experiment and that of Ma et al. (2001) is not clear from this study.

Enhanced degradation of MITC has been reported by several studies (Roberts and Stoydin, 1976; Mulder, 1995; Di Primo et al., 2003; Dungan and Yates, 2003). Enhanced degradation could be induced by a longer application history or by increasing pesticide dosages (Walker et al., 1986; Avidov et al., 1988). Enhanced degradation depends on the physical and chemical characteristics of the soil and fumigant (Verhagen et al., 1996). Higher application frequency increases the potential of adapted microbial populations for enhanced degradation (Smelt et al., 1989). However, these results have not been universally observed. Smelt et al. (1989) found 2 out of 25 tested soils did not exhibit enhanced degradation of MITC, even though they had 13+ years of MITC application. A faster degradation of MITC was observed only at 390 kg ha^{-1} MITC application rate in the fumigated nursery soil than in the corresponding forest soil in Wisconsin. No enhanced MITC degradation was observed in nursery soils. This was likely caused by the time period between the last fumigation in the sites and the time of soil sampling for this study longer than 2 to 3 yr, which has been cited as a time limit for the enhanced degradation effect (Verhagen et al., 1996). Different fumigants applied together could result in the reduction of stimulation to the growth of microorganisms that are responsible to enhanced degradation of a specific fumigant compound. The activity of fumigant-degrading microbes may decrease with increased elapsed time since the last fumigation.

Effects of Sterilization

Methyl isothiocyanate and CP degradation in sterilized soils was two to nine times slower than in the fresh soils (Fig. 2). In the two nursery soils, soil sterilization also significantly ($P \leq 0.05$) increased $t_{1/2}$ at 195 and 785 kg ha^{-1} application rates for MITC and at 140 and 560 kg ha^{-1} for CP (Fig. 2). Consistent differences in $t_{1/2}$ values of MITC and CP between fresh and sterilized soils suggested that the primary driver for fumigant transformation in fresh soils is soil microorganisms. The contribution of abiotic MITC transformation to the total degradation ranged from 10 to 35% in two sterilized nursery soils (Fig. 2). In sterilized Hayward nursery soil, CP showed no significant difference ($P \leq 0.05$) of degradation rates between three application rates (Fig. 2). The $t_{1/2}$ of CP at 560 kg ha^{-1} application rate in sterilized Byromville nursery soil was 7.6 d and abiotic CP degradation was significantly slower than at 140 and 280 kg ha^{-1} rates. A previous study indicated that CP was degraded predominantly by biodegradation in the soil, and $t_{1/2}$ of CP was 2.4 d in a sterilized Arlington sandy loam and increased 6.2 times in a fresh soil (Zheng et al., 2003).

The relative contribution of microbial degradation to total degradation of MITC and CP varied with nursery location and application rate in two nursery soils (Fig. 3). The biological portion of degradation was greater than 60% of total MITC degradation. The contribution of abiotic MITC degradation to the total degradation was only 10% in Wisconsin nursery soil at 390 kg ha^{-1} MITC application rate (Fig. 3). The contribution of microbial degradation to CP overall degradation ranged from 40 to 80% of the total degradation. Through abiotic pathway, CP can be transformed by reacting with iron-bearing clay minerals (Cervini-Silva et al., 2000).

There was no clear trend of the application rate dependence of MITC or CP degradation. The range of microbial degradation of two fumigants in our experiments was comparable to the literature, where 50 to 80% of the total degradation of MITC in one agricultural soil (Gan

Table 3. First-order rate constant (k) and half-life ($t_{1/2}$) of methyl isothiocyanate (MITC) and chloropicrin (CP) degradation in two fumigated nursery soils and two nonfumigated forest soils at three application rates of 195, 390, and 785 kg ha^{-1} for MITC and 140, 280, and 560 kg ha^{-1} for CP in incubation at 22°C.†

Site, application rate	Nursery soil		Forest soil	
	Rate constant (k), $\times 10^{-1}$	Half-life ($t_{1/2}$)	Rate constant (k), $\times 10^{-1}$	Half-life ($t_{1/2}$)
	d^{-1}	d	d^{-1}	d
		MITC		
Hayward, WI				
195 kg ha^{-1}	1.14 ± 0.15 (0.93)	6.09 a, A	1.52 ± 0.48 (0.90)	4.57 a, A
390 kg ha^{-1}	2.00 ± 0.18 (0.84)	3.47 a, A	0.62 ± 0.07 (0.91)	11.20 b, B
785 kg ha^{-1}	0.58 ± 0.13 (0.89)	11.91 a, B	2.21 ± 0.29 (0.88)	3.14 b, A
Byromville, GA				
195 kg ha^{-1}	1.67 ± 0.27 (0.91)	4.14 a, A	1.55 ± 0.12 (0.94)	4.46 a, A
390 kg ha^{-1}	1.68 ± 0.24 (0.88)	4.13 a, A	2.05 ± 0.21 (0.97)	3.38 a, A
785 kg ha^{-1}	1.38 ± 0.13 (0.83)	5.01 a, A	1.77 ± 0.45 (0.93)	3.91 a, A
		CP		
Hayward, WI				
140 kg ha^{-1}	2.26 ± 0.24 (0.86)	3.06 a, A	1.61 ± 0.06 (0.92)	4.31 a, A
280 kg ha^{-1}	4.81 ± 0.38 (0.97)	1.44 a, A	1.26 ± 0.32 (0.90)	5.51 b, A
560 kg ha^{-1}	1.54 ± 0.17 (0.79)	4.50 a, A	2.07 ± 0.23 (0.88)	3.34 a, A
Byromville, GA				
140 kg ha^{-1}	8.56 ± 0.79 (0.89)	0.81 a, A	3.46 ± 0.19 (0.87)	2.00 a, A
280 kg ha^{-1}	3.01 ± 0.31 (0.93)	2.31 a, A	8.25 ± 0.47 (0.92)	0.84 a, A
560 kg ha^{-1}	4.25 ± 0.28 (0.94)	1.63 a, A	2.75 ± 0.28 (0.91)	2.52 a, A

† Data are shown as the means of triplicate samples ± standard deviation. Values in parentheses are r^2, coefficients of fitting. Different letters indicate significant difference at $P < 0.05$ between nursery and forest soil at each application rate (lowercase) and three rates for each soil (uppercase), respectively, according to Tukey's Honestly Significant Difference (HSD) tests. The application rates represent 0.5×, 1×, and 2× recommended field application rates, respectively.

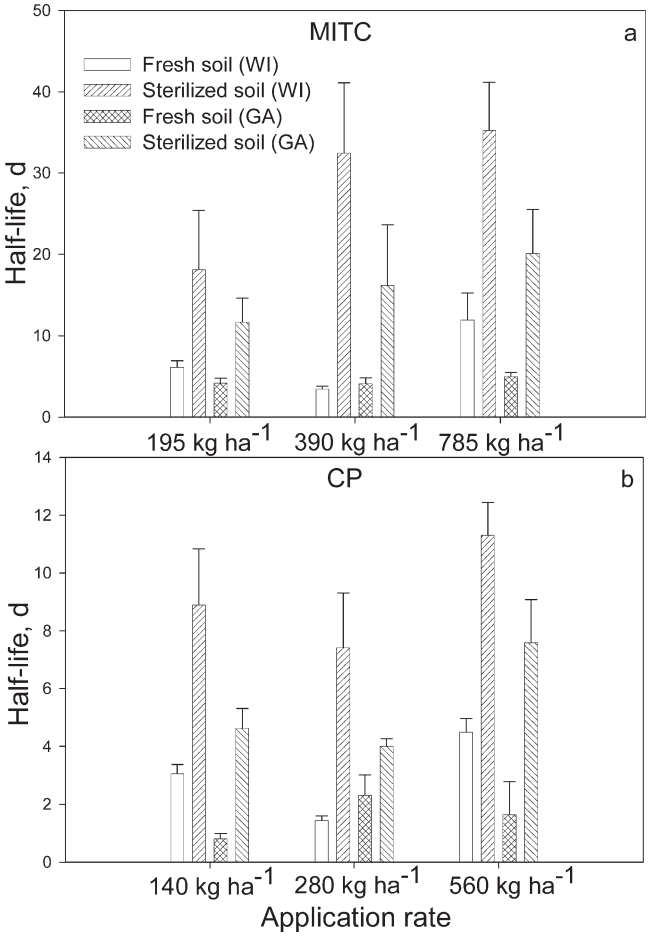

Fig. 2. Comparison of half-life ($t_{1/2}$) of (a) methyl isothiocyanate (MITC) and (b) chloropicrin (CP) at three application rates of 195, 390, and 785 kg ha^{-1} for MITC and 140, 280, and 560 kg ha^{-1} for CP in fresh soils and sterilized soils of two fumigated nursery soils in incubation at 22°C. Vertical bars are standard errors.

et al., 1999; Dungan et al., 2003), 68 to 92% of the overall CP degradation in three agricultural soils (Gan et al., 2000), and 84% of CP degradation in one fresh agricultural soil (Zheng et al., 2003) were attributed to microbial degradation. Similar to the previous studies, our results indicated that biodegradation played a primary role in overall degradation of MITC and CP in forest nursery soils.

Effects of Soil Moisture

In the air-dried Hayward nursery soil at the 390 kg ha^{-1} application rate, $t_{1/2}$ of MITC changed from 4.7 d at 0.5% to 3.4 d at 5%, 4.8 d at 10%, and 7.3 d at 15% moisture content (Fig. 4). The $t_{1/2}$ values of MITC in this study are consistent with those (3.3–9.9 d) of six soils at 20% moisture content (20°C) (Gerstl et al., 1977) and those (3.0–8.6 d) of two soils under impact of increasing soil moisture content from 1.8 to 16% (30°C) (Gan et al., 1999). A similar trend was found for CP at the 280 kg ha^{-1} rate, except the $t_{1/2}$ was about 2 d shorter than $t_{1/2}$ for MITC at corresponding moisture levels (Fig. 4). Analysis of variance results indicated that these $t_{1/2}$ values in the air-dried soil were not statistically different from the corresponding values in the fresh soil at 6.8% moisture content. There was also no significant impact of soil moisture on MITC and CP degradation so long as soil moisture was ≤10% (w/w).

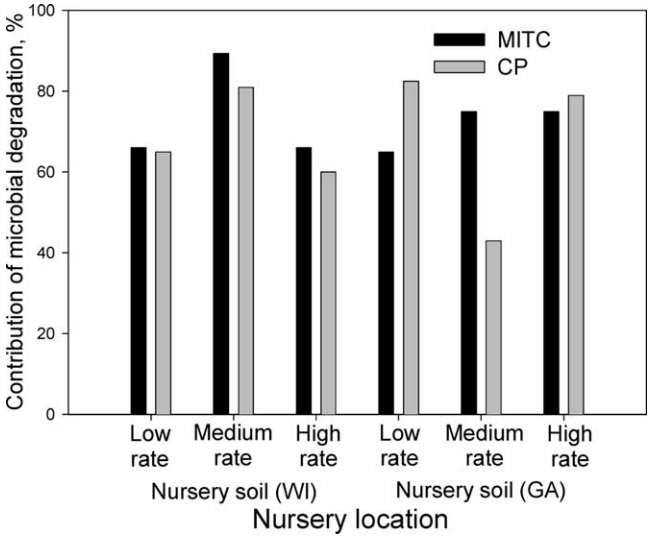

Fig. 3. Relative contribution of microbial degradation to total degradation of methyl isothiocyanate (MITC) and chloropicrin (CP) in two nursery soils at three application rates of 195, 390, and 785 kg ha^{-1} for MITC and 140, 280, and 560 kg ha^{-1} for CP.

Pesticide degradation generally increases with increasing soil moisture content (Gan et al., 1999). However, degradation of two fumigants showed the opposite trend in our experiments. The degradation of MITC and CP decreased when moistures increased from 5 to 15%. The statistical analysis at the $P < 0.05$ level suggested that only soil moisture at 15% significantly reduced degradation rates of MITC and CP compared to those at soil moisture contents of ≤10%. The $t_{1/2}$ of MITC and CP at 15% moisture was two to three times higher than those at 5 to 6.8% (w/w) in this nursery soil. For example, CP at 5% moisture degraded 2.3 times faster than at 15% moisture. The results of this experiment suggest that fumigant degradation was inhibited in soils of 15% moisture content. In a study by Gan et al. (1999), degradation of MITC showed a general decreasing trend as soil moisture water increased from 1.8 to 16% in Carsitas loamy sandy and Arlington sandy loam. Methyl isothiocyanate degradation at 16% moisture was 2.6 times slower than at 1.8% moisture in a Carsitas loamy sand (Gan et al., 1999). In Arlington soil, the greatest decrease ($P < 0.05$) of MITC degradation occurred when soil moisture content increased from 6 to 11% but degradation of 1,3-D isomers was not impacted by soil moisture content. In Carsitas soil, MITC degradation consistently decreased as moisture content increased from 1.8 to 11%, and remained the same as moisture content increased from 11 to 16%; degradation of two 1.3-D isomers linearly increased with increasing soil moisture content from 1.8 to 16%. The results of this study, Gan et al. (1999), and Gerstl et al. (1977) indicated the impact of soil moisture variation on fumigant degradation appeared dependent on fumigant and soil type.

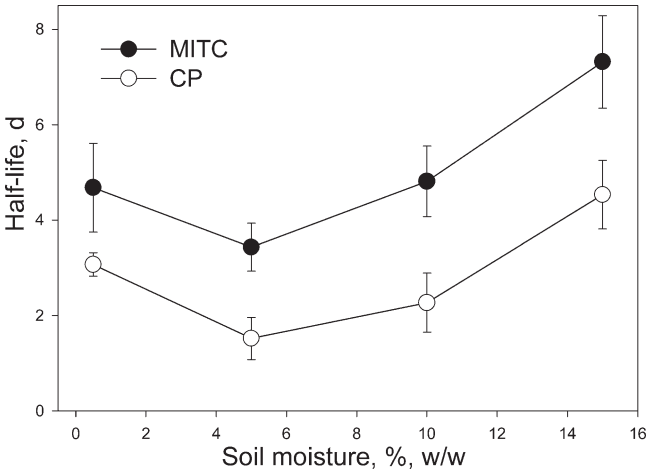

Fig. 4. Comparison of half-life ($t_{1/2}$) of methyl isothiocyanate (MITC) and chloropicrin (CP) at four moisture levels at 390 kg ha^{-1} for MITC and 280 kg ha^{-1} for CP in a nursery soil. The points are the means of triplicate samples (±standard errors).

CONCLUSIONS

Results of this study indicated that the degradation rates of MITC and CP varied considerably with nursery location and fumigant application rate. For each fumigant studied, no significant difference in degradation rates was found between the nursery soils with fumigation history and the forest soils without fumigation history. The values of the degradation rates of MITC and CP in the nursery soils are consistent with those in current literature on MITC and CP biodegradation in agricultural soils. Our experiments on soil moisture showed that MITC and CP degradation was virtually independent of moisture until soil moisture content exceeded 15% by weight.

The importance of microbial degradation was demonstrated by a consistent reduction in degradation rates when soils were sterilized. Microbial degradation accounted for >60% for MITC and 40 to 80% for CP of the overall degradation in two nursery soils. The behavior of microorganisms in soil could be evaluated more accurately by using field samples since cold storage of soils under freezing has documented effects on soil microbial diversities, populations, and activities. In this study, the freshly collected soils were used in incubation as soon as they were collected. This, being a unique aspect of the study, also led to large variations in measured $t_{1/2}$ compared to other published results where agricultural soils were air-dried, grinded to <2 mm, and stored under freezing conditions before analysis. This further emphasizes the key role of soil microorganisms in fumigant degradation, and suggests more microbiological study should focus on not only fumigants' effect on soil microbial community but also microbial transformation mechanisms of fumigants in soil.

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