Effect of Combined Application of Methyl Isothiocyanate and Chloropicrin on Their Transformation

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ABSTRACT

Combining several soil fumigants to increase the broad spectrum of pest control is a common fumigation practice in current production agriculture. In this study, we investigated the effect of combined application of chloropicrin and methyl isothiocyanate (MITC) on their transformations and persistence in the environment. In aqueous solution, no direct reaction between MITC and chloropicrin occurred and relatively slow rates of hydrolysis of these compounds were observed in aquatic environments free of suspended solids. The transformation of chloropicrin, however, was accelerated in aqueous solution with MITC because of a reduction reaction with bisulfide (HS⁻), which is a by-product of MITC hydrolysis. In soil, when fumigants were applied simultaneously, the degradation of MITC was suppressed under the bi-fumigant application due to the inhibition of soil microbial activity and a possible abiotic competition with chloropicrin for a limited number of reaction sites on the surface of soil particles. However, the degradation rate of chloropicrin was significantly enhanced in the bi-fumigant soil system, which was primarily attributed to the reaction of chloropicrin and HS⁻. Two sequential application approaches were developed to investigate the feasibility of the combined application of metam sodium (parent compound of MITC) and chloropicrin in soil and assess their potential effects on environmental fate. For both application sequences, the degradation of chloropicrin was accelerated and that of MITC, as a major breakdown product of metam sodium, was inhibited in soil.

SOIL FUMIGANTS have been used extensively for decades and will probably continue to serve as an effective strategy to control soil-borne pests in the near future. Methyl bromide (MeBr) is a popular and highly effective soil fumigant. However, MeBr is on an irreversible course for phase out in the United States and other developed countries because of its potential for deleting stratospheric ozone (USEPA, 2000). In addition to MeBr, only a few chemicals are currently registered for soil fumigation including chloropicrin, 1,3-dichloropropene (1,3-D), metam sodium, and dazomet. These alternative fumigants are more target pest specific and lack the broad-spectrum activity of MeBr in pest control. Additional chemicals (e.g., methyl iodide) are being developed as alternative fumigants, but uncertainties regarding the efficacy, environmental fate, and eco-

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nomics of use of these alternatives need to be addressed before they are registered for field application.

Much of the recent field research has focused on developing management practices for the existing soil fumigants to maintain crop yields and minimize environmental contamination. Combined application of alternative fumigants through drip irrigation systems has been demonstrated (Shaw and Larson, 1999; Trout and Ajwa, 1999; Ajwa et al., 2002). The simultaneous application of two or more fumigants is intended to broaden the spectrum of pest control activity in an attempt to achieve pest control efficacy and crop yield responses similar to that achieved by MeBr. For example, chloropicrin is an excellent fungicide but has much less activity against nematodes compared with 1,3-D and MeBr (Kreutzer, 1963). Thus, combinations of 1,3-D and chloropicrin have been developed as commercial formulations, including Telone C17 (17% chloropicrin) and Telone C35 (35% chloropicrin) (Dow AgroSciences, Indianapolis, IN). However, neither chloropicrin nor 1,3-D is effective in completely controlling weeds. An additional measure (such as application of herbicides) may be required to achieve the full spectrum of pest control activity provided by MeBr. The fumigant metam sodium or dazomet may provide effective weed control in addition to activity against plant pathogenic nematodes (Koster and van der Meer, 1990; Csinos et al., 1997; Duniway, 2002). Therefore, they are being proposed to be used in conjunction with the other two soil fumigants (1,3-D and chloropicrin) in an effort to provide greater or more consistent pest control (Duniway, 2002).

Once in contact with warm or moist soil, both metam sodium and dazomet decompose rapidly to MITC (Smelt et al., 1989; van den Berg et al., 1999), which is a general biocide used to control weeds and nematodes in soil. The conversion rate is very rapid (a few hours to a day) and the efficiency is very high (>90%), depending strongly on soil temperature, soil moisture, and soil texture (Turner and Corden, 1963; Smelt et al., 1989). Currently, metam sodium has been widely applied for production agriculture, and its total usage has consistently ranked third among all pesticides in the United States since 1995 (Donaldson et al., 2002). Great concern for the effect of metam sodium on the environment, public health, and aquatic organisms was associated with an event called "California's worst environmental disaster inland," in which approximately 72 000 L of 32.5% metam sodium was accidentally released into the upper Sacramento River in July, 1991 (California Environmental Protection Agency, 1992).

Unfortunately, chloropicrin and 1,3-D may react rapidly with metam sodium when they are combined in aqueous solution (Zheng et al., 2004), indicating that

simultaneous application of metam sodium and chloropicrin or 1,3-D may not be a feasible application technology for soil fumigation. To overcome the incompatibility, sequential application practices are being developed (Trout and Ajwa, 1999; Duniway, 2002; Zheng et al., 2004). Metam sodium will transform quickly to MITC in soil, thus sequential application separated in time can avoid the direct interaction between metam sodium and halogenated fumigants. The successful sequential application of fumigants may provide an improvement in crop yield, because chloropicrin and MITC target different plant pests and soil-borne pathogens (Duniway, 2002). Although there is no direct chemical reaction between MITC and chloropicrin, the influence of MITC as a major breakdown product of metam sodium or dazomet on the abiotic and biotic transformation of chloropicrin should be evaluated if the sequential fumigation practice is applied. Most of the current research related to the environmental fate of fumigants focuses on a single compound (Gan et al., 1999; Ma et al., 2001; Guo et al., 2003). To date, limited research pertaining to the environmental behavior of binary or multiple fumigants has been published (Zheng et al., 2003, 2004). Combined application of two or more pesticides may alter the microbial population and activity in soil (Stiles et al., 2000), which would result in a significant effect on their transformation and persistence in soil relative to that determined for a single chemical compound (Domsch et al., 1983). Additionally, the application of a binary fumigant formulation may also affect the rate of abiotic transformation because of competition for a limited number of reactive sites on the surface of soil particles (Zheng et al., 2003).

The objectives of this research were to characterize MITC and chloropicrin transformation in aqueous solution and soil, and to determine the influence of their combined application on the environmental persistence of the individual chemicals. To evaluate the combined effects on the transformation kinetics of MITC and chloropicrin in soil, three approaches were investigated: (i) simultaneous application of MITC and chloropicrin; (ii) sequential application of chloropicrin 2 wk before metam sodium (precursor of MITC); and (iii) sequential application of chloropicrin 3 d after metam sodium.

MATERIALS AND METHODS

Chemicals and Soil

Standards of chloropicrin (99%) and metam sodium (dihydrate, 99%) were purchased from Chem Service (West Chester, PA). Methyl isothiocyanate (MITC) was obtained from Sigma Chemical Co. (St. Louis, MO). All chemicals were used as received.

An Arlington sandy loam soil (coarse-loamy, mixed, thermic Haplic Durixeralf) used in the incubation study was collected from the University of California Agricultural Experiment Station in Riverside, CA. The soil had not been previously treated with soil fumigants. Fresh soil was passed through a 2.0-mm screen without air-drying and stored at low temperature (4°C) before use. The soil has a pH of 7.2 and contains 0.92% organic matter.

Experiments in Aqueous Solution

To understand the influence of combined fumigant application on persistence in aquatic environments, experiments to determine the rate of degradation of MITC and chloropicrin separately and in mixture were conducted in pH 6.9 buffer solution. In brief, stock solutions of chloropicrin and MITC were mixed in 125-mL serum bottles sealed with Teflon-faced butyl rubber septa and aluminum seals. The initial concentration of each fumigant was 1.8 mM. All samples were incubated in the dark at 25 ± 0.5°C. At regular time intervals, three 0.5-mL aliquots were removed from each flask using a gas-tight syringe and transferred into sealed glass vials containing ethyl acetate (3.0 mL) and anhydrous sodium sulfate (2.5 g). The vials were vigorously shaken for 10 min, and then an aliquot of the ethyl acetate was withdrawn and transferred to a gas chromatography (GC) vial for fumigant analysis. Control experiments were performed in the single fumigant solution to determine the rates of MITC and chloropicrin hydrolysis.

The concentration of chloropicrin and MITC was analyzed using a Hewlett-Packard (Palo Alto, CA) 6890 GC equipped with an on-column injector, a micro-electron capture detector (μ-ECD), a nitrogen–phosphorus detector (NPD), and a 30-m DB-VRX, 0.25-mm-i.d. × 1.4-μm-film-thickness fused-silica capillary column (J&W Scientific, Folsom, CA). The chromatographic conditions were 1.4 mL/min carrier gas flow rate (He), 240°C inlet temperature, and 290°C for both detectors. The initial oven temperature was 45°C for 1 min and the temperature was increased to 80°C at 2.5°C/min, then increased to 120°C at 30°C/min and held for 2 min. Under these conditions, the retention time of chloropicrin was 13.6 min (detected by ECD), and the retention time of MITC (analyzed simultaneously by NPD) was 11.1 min. Data were subjected to analysis of variance, and means were compared by least significant difference.

Hydrolysis products of MITC were extracted from the gas and aqueous phases and identified by GC–mass spectrometry (MS) to obtain information of the degradation of MITC in aqueous solution. The MITC solution (10 mM) was prepared in deionized water in a sealed glass vial, the pH was adjusted to 10.0, and the vial was placed in a water bath at 60°C. At appropriate time intervals, an aliquot of the solution was extracted with ethyl acetate, and analyzed by GC–MS. At each sampling time, a gas sample was withdrawn from the vial using a gas-tight syringe and injected into the GC–MS directly. Ethyl acetate extracts and gas phase samples were analyzed using a Hewlett-Packard (Palo Alto, CA) 5890 GC in tandem with a quadrupole HP 5971 mass selective detector equipped with an on-column injector and a DB-VRX capillary column. The electron impact (EI) mass spectra were generated using an electron energy of 70 eV and were monitored for ions m/z 20–300 for MITC hydrolysis products.

Experiments in Soil

The effects of combined application on fumigant transformations were investigated using an Arlington sandy loam with three types of approaches: a simultaneous application of MITC and chloropicrin, and two sequential applications of metam sodium and chloropicrin. For the simultaneous application of MITC and chloropicrin, 10 g of soil (dry weight, initial moisture 4.6%) were weighed into 20-mL glass vials. Solution (500 μL) containing a mixture of MITC and chloropicrin was injected into each vial, which was immediately capped with an aluminum seal and Teflon-faced butyl rubber septa. The initial concentrations of MITC and chloropicrin were 0.1, 0.6, and 1.8 mmol/kg in treated soil, which are representative of

concentrations occurring in fumigated field soils. All treated vials were incubated at $25 \pm 0.5°C$ in darkness. At intervals, triplicate samples were removed and stored at $-21°C$ until extraction. Extraction of soils was performed by adding anhydrous sodium sulfate (8 g) and ethyl acetate (10 mL) to vials while still frozen, sealing the vials immediately, vigorously shaking for 1 h, and vortexing for 2 min at room temperature. A portion of the ethyl acetate extract was transferred to a GC vial. The extract was analyzed by GC–ECD/NPD as described above. Soil samples containing only MITC or chloropicrin were prepared, incubated, extracted, and analyzed in the same way. Preliminary experiments indicated that the recovery of fumigant residues was >95% using this procedure. Disappearance of fumigants in soils was fitted to a first-order kinetic model. The degradation rate constants of fumigants were compared using a t test at a significance of $P = 0.05$ to test for differences in degradation rates in single-component and bifumigant soil systems.

The influence of combined application of fumigants on the rate of abiotic and biotic transformation of MITC and chloropicrin was determined using sterilized soils. Soil (10 g) was weighed into headspace vials, and then autoclaved twice at $121°C$ for 1 h with a 1-d interval between the first and second autoclaving. Sterilized soils were treated aseptically with 0.6 mmol/kg MITC, chloropicrin, and their mixture. The procedures described above were used for incubation, extraction, and analysis of residual fumigants.

For sequential applications, two sequentially applied orders were preformed: (i) application of metam sodium 2 wk after chloropicrin and (ii) application of chloropicrin 3 d after metam sodium. Briefly, 10 g of soil with 4.7% water content was treated with chloropicrin at 0.6 mmol/kg and then incubated at 25°C for 2 wk in the dark. Metam sodium (0.6 mmol/kg) was then injected into these chloropicrin-treated samples. Samples were additionally incubated at 25°C for 1 and 5 d, when triplicate vials were removed and extracted for fumigant determination. An additional set of vials was treated with 0.6 mmol/kg of metam sodium and incubated for 3 d at 25°C, after which chloropicrin (0.6 mmol/kg) was added and the samples incubated at 25°C for an additional 5 and 10 d. Samples were extracted and analyzed according to the procedures described above.
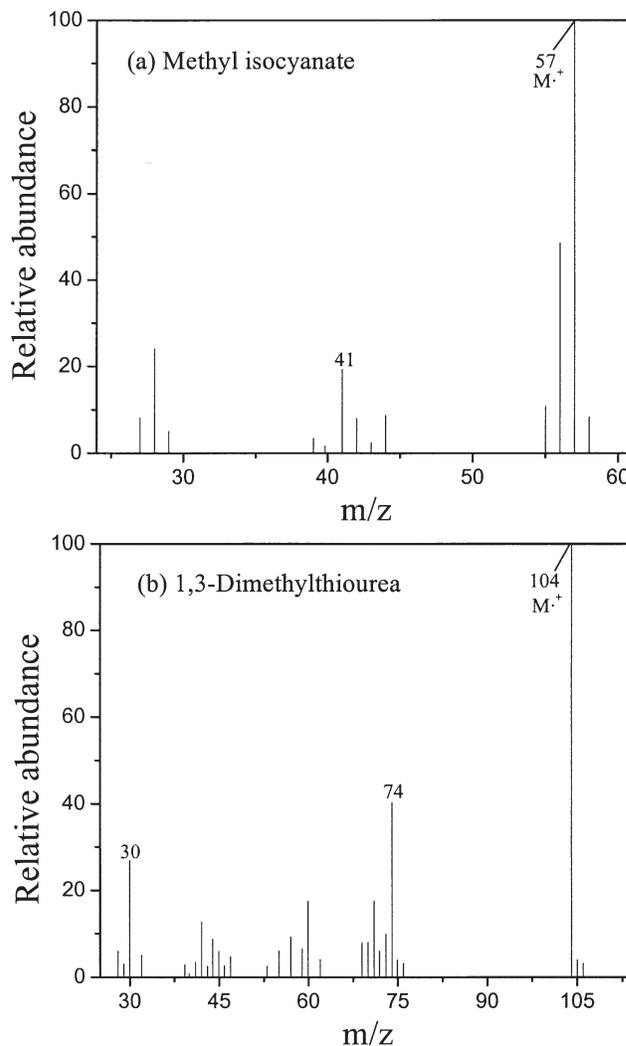

Fig. 1. Mass spectra (electron impact, EI) of hydrolysis products of methyl isothiocyanate (MITC): (a) methyl isocyanate and (b) 1,3-dimethylthiourea.

RESULTS AND DISCUSSION

Transformation of MITC and Chloropicrin in Aqueous Solution

Initial experiments focused on investigating the hydrolysis of MITC and chloropicrin and their transformation in binary-fumigant buffer solution (pH = 6.9). Both MITC and chloropicrin were stable in neutral aqueous solution at an initial concentration of 1.8 mM. The hydrolysis half-lives ($t_{1/2}$) of MITC and chloropicrin were approximately 93 and 83 d, respectively. This observation is consistent with other reports that MITC and chloropicrin undergo extremely slow hydrolysis without light and microorganisms in the neutral aqueous solution (Castro and Belser, 1981; Wilhelm et al., 1996; Wales, 2000).

Degradation half-life of MITC determined in binary-fumigant buffer solution was approximately 95 d at an initial concentration of 1.8 mM, which suggested that the persistence of MITC was not significantly altered by the presence of chloropicrin. It verifies that no direct interaction occurred between MITC and chloropicrin in aqueous solution. In contrast, chloropicrin disappeared more rapidly in a fumigant mixture with MITC than in solution containing only chloropicrin, with a degradation half-life at 43 d for chloropicrin approximately two times lower compared with hydrolysis. These results suggest that the increased dissipation of chloropicrin in mixture with MITC was probably due to reaction of chloropicrin with certain MITC hydrolysis products, such as nucleophilic sulfur species.

To further investigate the enhanced chloropicrin transformation in mixture with MITC, we identified some of the hydrolysis products of MITC. Following hydrolysis of MITC in a sealed vial under alkali condition, an aliquot of the headspace was withdrawn using a gas-tight syringe and directly analyzed by GC–MS. Simultaneously, a solution sample was removed and extracted with ethyl acetate for analysis by GC–MS. Two primary hydrolysis products were characterized: methyl isocyanate was identified in the gas sample (Fig. 1a), and 1,3-dimethylthiourea was present in the
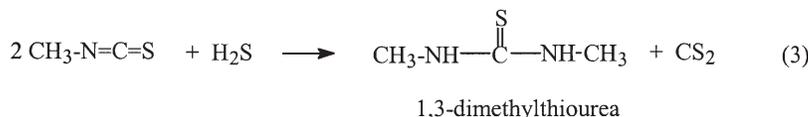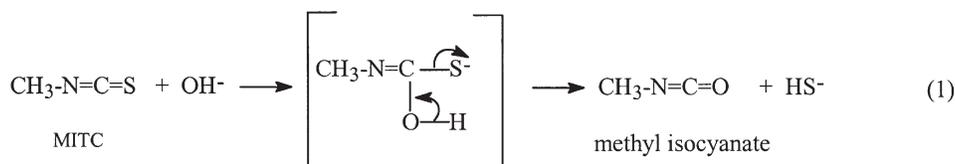
$$CH_3\text{-}N\text{=}C\text{=}S \ + \ OH^- \ \longrightarrow \ \left[\begin{array}{c} CH_3\text{-}N\text{=}C \underset{O\text{---}H}{\overset{S^-}{\big|}} \end{array} \right] \longrightarrow \ CH_3\text{-}N\text{=}C\text{=}O \ \ + \ HS^- \qquad (1)$$

MITC　　　　　　　　　　　　　　　　　　　　　　　　　　　methyl isocyanate

$$HS^- \ + \ H_2O \ \rightleftharpoons \ H_2S \ + \ OH^- \qquad (2)$$

$$2\ CH_3\text{-}N\text{=}C\text{=}S \ \ + \ H_2S \ \longrightarrow \ CH_3\text{-}NH\overset{\overset{\displaystyle S}{\|}}{\text{---}C\text{---}}NH\text{-}CH_3 \ + \ CS_2 \qquad (3)$$

1,3-dimethylthiourea

Fig. 2. Chemical reactions associated with products of MITC hydrolysis in basic solution.

extract of the hydrolysis solution (Fig. 1b). Chemical reactions associated with these products of MITC hydrolysis in basic solution are outlined in Fig. 2.

Figure 2 indicates that the hydrolysis of MITC yields methyl isocyanate and bisulfide (HS^-). Bisulfide may be transformed to hydrogen sulfide (H_2S) species, which can further react with MITC to form 1,3-dimethylthiourea (Joris et al., 1970; Turner and Corden, 1963). Dimethylthiourea has also been detected as an intermediate in the hydrolysis of metam sodium (Draper and Wakeham, 1993). We propose that the formation of HS^- during MITC hydrolysis played a crucial role in accelerating the transformation of chloropicrin in aqueous solution. Bisulfide is not only a highly reactive nucleophile that may undergo bimolecular nucleophilic substitution (S_N2) with halogenated compounds to form organic sulfur compounds (Barbash and Reinhard, 1989; Roberts et al., 1992), but also a reductant that may destroy polyhalogenated hydrocarbons via a redox process (Kriegman-King and Reinhard, 1992; Perlinger et al., 1996). The mild oxidation potential of chloropicrin makes it susceptible to withdraw electrons from the electron donors (such as bisulfide) and degrade via a successive dechlorination process (Cl_3CNO_2 + HS^- = Cl_2CHNO_2 + S + Cl^-; Cl_2CHNO_2 + HS^- = $ClCH_2NO_2$ + S + Cl^-). Similar transformation processes of chloropicrin were also observed in other sulfur species solutions,

for example, sulfite (Croue and Reckhow, 1989) and metam sodium (Zheng et al., 2004). Therefore, a redox reaction between HS^- and chloropicrin may have occurred in aqueous solution containing both chloropicrin and MITC, resulting in an increased degradation rate of chloropicrin. These results imply that the occurrence of chloropicrin with MITC in aquatic environments would alter the persistence of chloropicrin and reduce its residue in the ecosystem.

Competitive Degradation between MITC and Chloropicrin in Soil

The effect of combined application of chloropicrin and MITC on their fate was determined in Arlington sandy loam. In general, the dissipation of fumigants following field application is largely attributed to volatilization and degradation. However, the dissipation of MITC and chloropicrin in the experimental system is believed to be governed by abiotic and biotic degradation. The rate of chloropicrin or MITC degradation depended in principle on the initial concentration (Tables 1 and 2). For example, the degradation rate of chloropicrin decreased by approximately 40 times when the initial concentration was increased from 0.1 to 1.8 mmol/kg in the absence of MITC.

The degradation of MITC was suppressed for all ini-

Table 1. Pseudo-first-order rate constants (k) of methyl isothiocyanate (MITC) degradation in Arlington sandy loam with and without chloropicrin.

MITC	Chloropicrin	$k \times 10^2$	r^2†	Inhibition
——— mmol/kg ———		d^{-1}		%
0.1	0	29.6 ± 0.8	0.991	37.6
0.1	0.1	18.5 ± 0.3*	0.996	
0.6	0	10.7 ± 0.1	0.997	40.6
0.6	0.6	6.32 ± 0.21*	0.982	
1.8	0	5.88 ± 0.20	0.981	41.7
1.8	1.8	3.43 ± 0.13*	0.975	
0.6 (sterile soil)	0	3.91 ± 0.25	0.903	12.9
0.6 (sterile soil)	0.6	3.40 ± 0.31*	0.889	

* The degradation rate constants of MITC in the presence and absence of chloropicrin are significantly different at the 0.05 probability level.
† Correlation coefficient of fitting.

Table 2. Pseudo-first-order rate constants (k) of chloropicrin degradation in Arlington sandy loam with and without methyl isothiocyanate (MITC).

Chloropicrin	MITC	$k \times 10$	r^2†	Acceleration
——— mmol/kg ———		d^{-1}		%
0.1	0	18.3 ± 1.5	0.978	8.5
0.1	0.1	19.9 ± 1.4	0.984	
0.6	0	1.39 ± 0.08	0.951	54.7
0.6	0.6	2.15 ± 0.11*	0.971	
1.8	0	0.44 ± 0.03	0.925	84.5
1.8	1.8	0.81 ± 0.03*	0.985	
0.6 (sterile soil)	0	0.56 ± 0.07	0.886	105.4
0.6 (sterile soil)	0.6	1.15 ± 0.08*	0.966	

* The degradation rate constants of chloropicrin in the presence and absence of MITC are significantly different at the 0.05 probability level.
† Correlation coefficient of fitting.

tial concentrations when the fumigant was applied to soil in combination with chloropicrin (Fig. 3). For instance, combined fumigant application resulted in a degradation rate for MITC approximately 37 to 42% less than that for MITC alone. Therefore, MITC may be more persistent in soil when it is applied with chloropicrin. A possible potential outcome of MITC degradation inhibition would be a reduction of the MITC application rate because the fumigant activity was prolonged in soil. Given that MITC dissipation in soil is a comprehensive process of abiotic and biotic degradation (Gan et al., 1999), its reduced degradation rate in applications with chloropicrin may have resulted from an inhibited soil microbial activity and competition for a limited number of reaction sites on the surface of soil particles. Previous studies have shown that fumigant application to soil can alter soil microbial communities and affect microbial activity (Stiles et al., 2000; Dungan et al., 2003; Ibekwe et al., 2001). Introduction of anthropogenic chemicals can usually result in an immediate inhibition of soil microbial activity, followed by a recovery or rebound period once the exterior effect is suspended. Previous research using mixtures of chloropicrin and 1,3-D suggested that chloropicrin and its degradation products may inhibit the activity of soil microorganisms and slow the transformation of *trans*-1,3-D (Zheng et al., 2003). The results of the experiment suggest that chloropicrin may have a similar affect on MITC-degrading microorganisms. The rate of MITC degradation in sterile soils with and without chloropicrin was lower than that in nonsterile soils (Table 1), suggesting an important role of microbiological processes in MITC degradation. The 12.9% reduction in the rate of MITC degradation in mixture with chloropicrin compared with MITC alone in sterile soil (Table 1) may be due to a competitive degradation process between MITC and chloropicrin on the surface of soil particles, similar to that described for 1,3-D and chloropicrin (Zheng et al., 2003).

The behavior of chloropicrin in combined application with MITC showed different trends than those observed for MITC. The disappearance of chloropicrin in the presence of MITC was significantly accelerated in comparison with the dissipation in soil spiked with chloropicrin only (Fig. 3). A larger increase in the chloropicrin degradation rate was observed with increasing initial fumigant concentration in soil (Table 2). Previous reports showed that MITC could inhibit the soil microbial activity and prolong the persistence of herbicides such as EPTC and pebulate in soil (Stiles et al., 2000). Our results for combined application of MITC and chloropicrin indicated the occurrence of a specific reaction that overwhelmed the effect of any possible inhibition of biotic degradation of chloropicrin by MITC. Since no direct chemical reaction between MITC and chloropicrin is expected, it can be deduced that MITC degradation products may rapidly react with chloropicrin and accelerate chloropicrin dissipation in soil. Bisulfide (HS⁻) as a degradation product of MITC (Fig. 2) could facilitate chloropicrin reduction via a dechlorination reaction and result in a rapid dissipation of chloropicrin in the bi-fumigant soil system.
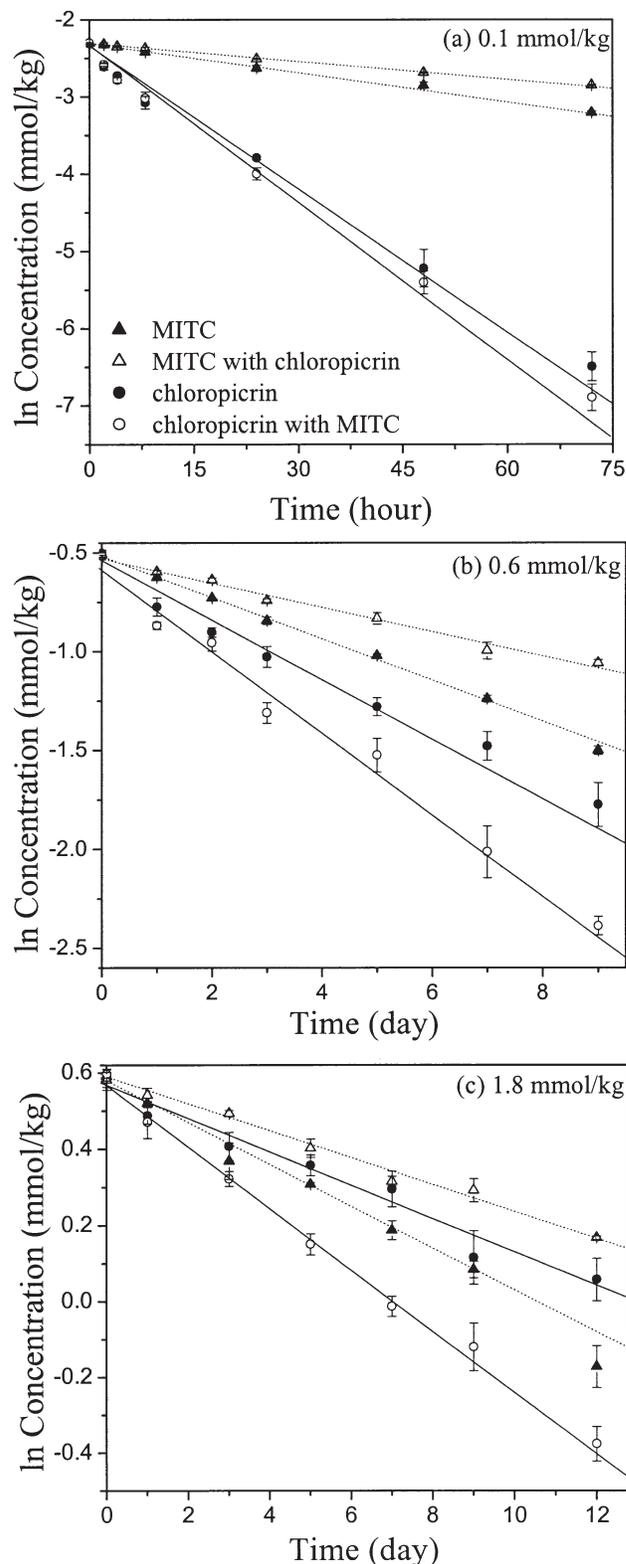

Fig. 3. Influence of binary-fumigant application on degradation rates in Arlington sandy loam at three initial concentrations. The dashed line represents the degradation of methyl isothiocyanate (MITC) and the solid line is chloropicrin.

The larger difference of chloropicrin degradation in the single and binary fumigant systems was observed in the sterile soil (Table 2). The difference of chloropicrin

degradation rate in the sterile soil is only attributed to abiotic factors, and it is an integrated result of the reduction transformation of chloropicrin by bisulfide and the possible competitive degradation with MITC on the surface of soil particles. Although the clay mineral and soil organic matter contain various high reactive groups and catalytic coupling sites (Weber and Huang, 2003), a limited number of reactive sites on the surface of soil particles may result in a competitive degradation between MITC and chloropicrin. However, the rapid redox reaction of chloropicrin with MITC degradation products such as HS^- made the competitive process insignificant.

Sequential Application of Metam Sodium and Chloropicrin to Soil

Sequential application of metam sodium and chloropicrin included two approaches differing in the order of fumigant application. In one approach, chloropicrin is applied first, followed by metam sodium when chloropicrin has achieved its pest control. Figure 4 displays the influence of combined fumigant application on the dissipation and residues of chloropicrin and MITC in soil under this sequential application approach. After the chloropicrin treatment of 14 d, the concentration of chloropicrin in soil was 0.071 ± 0.03 mmol/kg, equivalent to 12% of the initial fumigant application rate (0.6 mmol/kg). After the addition of metam sodium, the concentration of chloropicrin in soil was significantly decreased. The concentration of chloropicrin remaining in soil was reduced by approximately 70% in samples treated with metam sodium 1 d; at 5 d after metam sodium application, <3% chloropicrin residues in soil was determined compared with the chloropicrin concentration in samples receiving only chloropicrin (Fig. 4a). These results indicated that the rapid reduction reaction of chloropicrin by metam sodium could eliminate chloropicrin residues in soil and mitigate the potential risk to the environment.

Sequential application (chloropicrin followed by metam sodium) improved the availability of MITC in soil. The concentration of MITC was increased by approximately 5 and 33% 1 and 5 d after metam sodium application to chloropicrin-treated soil (Fig. 4b). Higher concentration of MITC in this bi-fumigant application system is due to both the transformation reaction of metam sodium with chloropicrin and the inhibition of MITC degradation by chloropicrin. The primary product of metam sodium reaction with chloropicrin is MITC (Zheng et al., 2004), and this transformation may contribute to the increase in MITC concentration first day following application of metam sodium to chloropicrin-treated soil. The influence of chloropicrin on MITC degradation by the inhibition of MITC-degrading microorganisms and the competition of reactive sites on the surface of soil particles may provide the major contribution to the increase in MITC concentration in soil 5 d after metam sodium addition. The increasing availability of MITC suggests that its environmental persistence may be increased in soil if the sequential fumigant application approach is used.
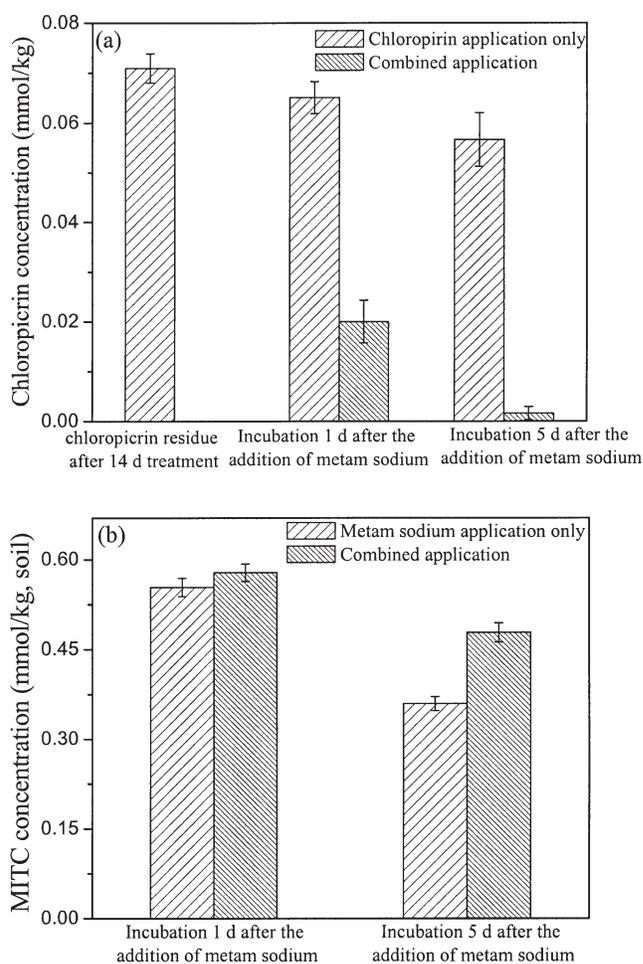

Fig. 4. Effect of fumigant sequential application on the dissipation of (a) chloropicrin and (b) methyl isothiocyanate in soil. Chloropicrin was applied 14 d followed by metam sodium, and then incubated for 1 and 5 d at $25 \pm 0.5°C$.

Another sequential application approach is to apply metam sodium a few days before an application of chloropicrin. Figure 5 depicts the influence of this sequential application on the behavior of chloropicrin and MITC in soil. Although >90% metam sodium was converted to MITC in Arlington sandy loam within the first day, chloropicrin was added after 3 d to allow metam sodium adequate time for complete conversion to MITC. The dissipation of MITC was measured 5 and 10 d after chloropicrin addition, and indicated that MITC degradation was inhibited in soil receiving both metam sodium and chloropicrin compared with that receiving metam sodium alone (Fig. 5a). For example, the concentration of MITC in soil accounted for 47% of the applied metam sodium 10 d after chloropicrin application to metam sodium–treated soil, but only 29% for soil treated with metam sodium only. These results further suggest that chloropicrin may retard the dissipation of MITC by inhibiting biotic degradation and competing for abiotic transformation sites on the surface of soil particles, such as –NH$_2$, –NH–, –SH, and –OH reactive groups.

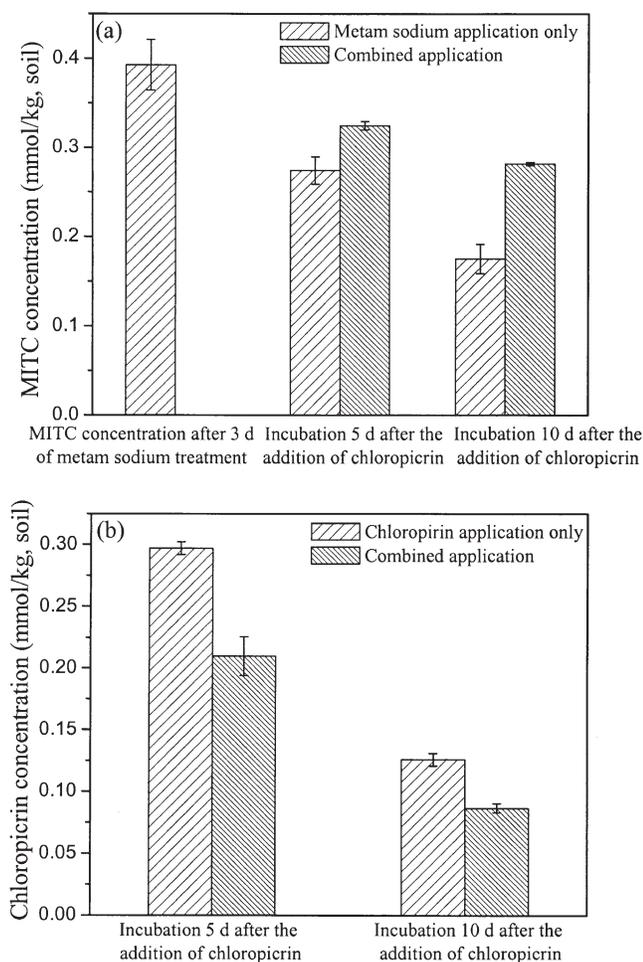The degradation of chloropicrin in the sequential ap-

Fig. 5. Effect of fumigant sequential application on the dissipation of (a) methyl isothiocyanate (MITC) and (b) chloropicrin in soil. Metam sodium was applied 3 d followed by chloropicrin, and then incubated for 5 and 10 d at 25 ± 0.5°C.

plication system was accelerated after 5 and 10 d of incubation compared with application of chloropicrin alone (Fig. 5b). Since metam sodium had completely dissipated within the 3 d before chloropicrin addition, no direct contact of chloropicrin and metam sodium occurred. Rather, an initial product of metam sodium degradation, bisulfide ($CH_3NHCSS^- \rightarrow CH_3NCS + HS^-$), could undergo redox reaction with chloropicrin. Degradation of MITC could also produce HS^- to further facilitate the transformation of chloropicrin in soil.

Overall, sequential application of metam sodium and chloropicrin should be a feasible practice for soil fumigation to avoid the rapid reaction that may occur during a simultaneous application. Two sequential application approaches exist. These approaches require further consideration to determine their effect on pest control, human health, economics, and the risk of environmental contamination. Duniway (2002) reported that the sequential application of shank injection of chloropicrin or Telone C35 followed by metam sodium provided strawberry yields nearly equivalent to standard fumigation with MeBr and chloropicrin. Although this sequential application approach requires more time to com-

plete a fumigation compared with application of metam sodium followed by chloropicrin, it is very attractive from the point of environment and economics. This sequential application practice has the potential to eliminate chloropicrin residues in soil because the reaction mechanism of chloropicrin with metam sodium is similar to the degradation of chloropicrin itself in the environment via reductive dehalogenations (Zheng et al., 2004). In addition, this fumigation practice increases the conversion yield of metam sodium and prolongs the persistence of MITC in soil. A potential outcome would be reduction of metam sodium application rates if the fumigant is to be used with chloropicrin according to this sequential fumigation approach. Further research is needed to evaluate the potential of decreased metam sodium rates for comparable pesticidal activity.

REFERENCES

Ajwa, H.A., T. Trout, J. Mueller, S. Wilhelm, S.D. Nelson, R. Soppe, and D. Shatley. 2002. Application of alternative fumigants through drip irrigation systems. Phytopathology 92:1349–1355.

Barbash, J.E., and M. Reinhard. 1989. Abiotic dehalogenations of 1,2-dichloroethane and 1,2-dibromoethane in aqueous solution containing hydrogen sulfide. Environ. Sci. Technol. 23:1349–1358.

California Environmental Protection Agency. 1992. Evaluation of the health risks associated with the metam spill in the Upper Sacramento River. Office of Environ. Health Hazard Assessment, Berkeley, CA.

Castro, C.E., and N.O. Belser. 1981. Photohydrolysis of methyl bromide and chloropicrin. J. Agric. Food Chem. 29:1005–1008.

Croue, J.-P., and D.A. Reckhow. 1989. Destruction of chlorination byproducts with sulfite. Environ. Sci. Technol. 23:1412–1419.

Csinos, A.S., W.C. Johnson, A.W. Johnson, D.R. Sumner, R.M. McPherson, and R.D. Gitaitis. 1997. Alternative fumigants for methyl bromide in tobacco and pepper transplant production. Crop Prot. 16:585–594.

Domsch, K.H., G. Jagnow, and T.-H. Anderson. 1983. An ecological concept for the assessment of side-effects of agrochemicals on soil microorganisms. Residue Rev. 86:65–105.

Donaldson, D., T. Kiely, and A. Grube. 2002. Pesticide industry sales and usage 1998 and 1999 market estimates. Office of Prevention, Pesticides, and Toxic Substances, USEPA, Washington, DC.

Draper, W., and D.E. Wakeham. 1993. Rate constants for metam sodium cleavage and photodecomposition in water. J. Agric. Food Chem. 41:1129–1133.

Dungan, R.S., A.M. Ibekwe, and S.R. Yates. 2003. Effect of propargyl bromide and 1,3-dichloropropene on microbial communities in an organically amended soil. FEMS Microbiol. Ecol. 43:75–87.

Duniway, J.M. 2002. Status of chemical alternative to methyl bromide for pre-plant fumigation of soil. Phytopathology 92:1337–1343.

Gan, J., S.K. Papiernik, S.R. Yates, and W.A. Jury. 1999. Temperature and moisture effects on fumigant degradation in soil. J. Environ. Qual. 28:1436–1441.

Guo, M., S.K. Papiernik, W. Zheng, and S.R. Yates. 2003. Formation and extraction of persistent fumigant residues in soils. Environ. Sci. Technol. 37:1844–1849.

Ibekwe, A.M., S.K. Papiernik, J. Gan, S.R. Yates, C. Yang, and D.E. Crowley. 2001. Impact of fumigants on soil microbial communities. Appl. Environ. Microbiol. 67:3245–3257.

Joris, S.J., K.I. Aspila, and C.L. Chakrabarti. 1970. Decomposition of monoalkyl dithiocarbamates. Anal. Chem. 42:647–651.

Koster, A.Th.J., and L.J. van der Meer. 1990. Effects of sheeting with black plastic or flooding of soils on the control of Cyperus esculentus. Acta Hortic. 266:569–573.

Kreutzer, W.A. 1963. Selective toxicity of chemicals to soil micro-organisms. Annu. Rev. Phytopathol. 1:101–126.

Kriegman-King, M.R., and M. Reinhard. 1992. Transformation of carbon tetrachloride in the presence of sulfide, biotite, and vermiculite. Environ. Sci. Technol. 26:2198–2206.

Ma, Q.L., J. Gan, S.K. Papiernik, J.O. Becker, and S.R. Yates. 2001. Degradation of soil fumigants as affected by initial concentration and temperature. J. Environ. Qual. 30:1278–1286.

Perlinger, J.A., W. Angst, and R.P. Schwarzenbach. 1996. Kinetics of the reduction of hexachloroethane by juglone in solutions containing hydrogen sulfide. Environ. Sci. Technol. 30:3408–3417.

Roberts, A.L., P.N. Sanborn, and P.M. Gschwend. 1992. Nucleophilic substitution reaction of dihalomethanes with hydrogen sulfide species. Environ. Sci. Technol. 26:2263–2274.

Shaw, D.V., and K.D. Larson. 1999. A meta-analysis of strawberry yield response to preplant soil fumigation with combination of methyl bromide-chloropicrin and four alternative systems. HortScience 34:839–845.

Smelt, J.H., S.J.H. Crum, and W. Teunissen. 1989. Accelerated transformation of the fumigant methyl isothiocyanate in soil after repeated application of metham-sodium. J. Environ. Sci. Health Part B B24:437–455.

Stiles, C.L., C.E. Sams, D.K. Robinson, D.L. Coffey, and T.C. Mueller. 2000. Influence of metam sodium on the dissipation and residual biological activity of the herbicides EPTC and pebulate in surface soil under black plastic mulch. J. Agric. Food Chem. 48:4681–4686.

Trout, T., and H.A. Ajwa. 1999. Strawberries response to fumigants applied by drip irrigation systems. Abstract 10. *In* Annu. Int. Res. Conf. Methyl Bromide Alternatives and Emissions Reductions, San Diego, CA. 1–4 Nov. 1999. Agric. Res. Consulting, Fresno, CA.

Turner, N.J., and M.E. Corden. 1963. Decomposition of sodium *N*-methyldithiocarbamate in soil. Phytopathology 53:1388–1394.

USEPA. 2000. Protection of stratospheric ozone: Incorporation of Clean Air Act Amendments for reductions in Class I, Group VI controlled substances. Fed. Regist. 65:70795–70804.

Van den Berg, F., J.H. Smelt, J.J.T.I. Boesten, and W. Teunissen. 1999. Volatilization of methyl isothiocyanate from soil after application of metam-sodium with two techniques. J. Environ. Qual. 28:918–928.

Wales, P.C. 2000. Evaluation of methyl isothiocyanate as a toxic air contaminant. California Environ. Protection Agency, Sacramento, CA.

Weber, W.J., and Q. Huang. 2003. Inclusion of persistent organic pollutants in humification processes: Direct chemical incorporation of phenanthrene via oxidative coupling. Environ. Sci. Technol. 37:4221–4227.

Wilhelm, S.N., K. Shepler, L.J. Lawrence, and H. Lee. 1996. Environmental fate of chloropicrin. p. 79–93. *In* J.N. Seiber et al. (ed.) Fumigant: Environmental fate, exposure, and analysis. ACS Symp. Ser. 652. Am. Chem. Soc., Washington, DC.

Zheng, W., S.K. Papiernik, M. Guo, and S.R. Yates. 2003. Competitive degradation between fumigants chloropicrin and 1,3-dichloropropene in unamended and amended soils. J. Environ. Qual. 32:1735–1742.

Zheng, W., S.R. Yates, M. Guo, S.K. Papiernik, and J.H. Kim. 2004. Transformation of chloropicrin and 1,3-dichloropropene by metam sodium in a combined application of fumigants. J. Agric. Food Chem. 52:3002–3009.