Competitive Degradation between the Fumigants Chloropicrin and 1,3-Dichloropropene in Unamended and Amended Soils

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ABSTRACT

The mixture of 1,3-dichloropropene (1,3-D) and chloropicrin (CP) is used as a preplant soil fumigant. In comparison with individual fumigants, application of a mixture may affect the environmental dissipation and fate of each chemical, such as emission and degradation. We investigated the degradation of CP, 1,3-D, and their mixture in fresh soils and sterile soils, and evaluated the competitive characteristic of fumigants in the mixture. The degradation of low concentrations of CP in fresh soil was accelerated at early times in the presence of 1,3-D, whereas the addition of CP reduced the degradation rate of *trans*-1,3-D, possibly by inhibiting the activity of *trans*-1,3-D degrading microorganisms. The potential of applying amendments to the soil to increase the rate of CP and 1,3-D degradation was also illustrated. The degradation of both fumigants was significantly enhanced in soils amended with ammonium thiosulfate (ATS) and sodium diethyldithiocarbamate (Na-DEDTC) compared with unamended soil. Competitive degradation was observed for CP in amended soils in the presence of 1,3-D. The degradation of *cis*-1,3-D in amended soils spiked as a mixture of 1,3-D and CP was repressed compared with the rate of degradation in samples spiked with 1,3-D only. This implied that in abiotic degradation, CP and *cis*-1,3-D competed for a limited number of reaction sites in amended soil, resulting in decreased degradation rates. No significant influence of fumigant mixtures was observed for *trans*-1,3-D in amended soil.

Methyl bromide (MeBr) is a widely used and very effective fumigant, which is applied to control soilborne pests in many high cash value crops such as strawberry and tomato. Due to the current scientific opinion that MeBr contributes significantly to the depletion of stratospheric ozone, its production and importation are being phased out as mandated by the U.S. Clean Air Act and the Montreal Protocol (USEPA, 2000). However, current agricultural practices require fumigation as a core component of soil pest management. The elimination of MeBr has led to an intense research effort to identify chemical alternatives to MeBr and to develop better management practices that would provide adequate pest control at an acceptable cost. 1,3-Dichloropropene (1,3-D) formulated with chloropicrin (CP) has been considered a likely alternative fumigant to MeBr in many field situations (Stephens, 1996; Moldenke and Thies, 1996). Mixtures of 1,3-D with 17% CP (i.e., Telone C-17) and 35% CP (i.e., Telone C-35) (Dow AgroSciences, Indianapolis, IN) have been developed as commercial formulations.

Fumigants have high vapor pressures and are transported predominantly in the vapor phase. Excessive emissions of their vapor into the atmosphere may contribute to air pollution and cause adverse effects on human and environmental health. Because many fumigants have acute and chronic toxicity, genotoxicity, or carcinogenicity, their emissions have caused wide concern and excessive concentrations in air have triggered restrictions of their use. For instance, high 1,3-D concentrations were detected in the ambient air near fumigated fields in 1990, resulting in a four-year suspension of 1,3-D use in California (California Department of Food and Agriculture, 1990). Airborne levels of CP determined during and after a preplant soil fumigation showed that workers might be exposed to high CP concentrations (Maddy et al., 1983, 1984). Because of the low sorption capacity of these compounds in soil, 1,3-D and CP are also potential sources of ground water contamination.

To minimize these negative effects of the fumigant on the environment, it is necessary to develop efficient management strategies to control fumigant emission and possible leaching. Experimental studies in the field and laboratory indicate that fumigant emission can be reduced by increasing application depth (Yates et al., 1997; Wang et al. 2001), covering the field with low-permeability plastic films (Wang et al., 1997; Papiernik et al., 2001), increasing the soil water content (Gan et al., 1996), and decreasing the application dosage. Deep application and surface tarping prolong fumigant residence times in soil, which may enhance soilborne pest control efficacy. These practices also increase the time for degradation in the soil, thereby reducing the amount of fumigant released into the atmosphere. Because the rate of fumigant degradation in soil is concentration-dependent (Ma et al., 2001), reducing the application rate not only directly decreases the total amount of fumigant available for volatilization loss, but may also reduce emissions by increasing the degradation rate.

Ideally, the fumigant will be completely destroyed by degradation in the soil once adequate pest control is achieved. However, in general, the fumigant degradation rate is relatively slow in comparison with its rapid vapor diffusion. Therefore, it may be important to manipulate and modify fumigant degradation to decrease harmful effects such as emission and leaching. Generally, soil chemical and biological conditions influence the rate of fumigant degradation in soil. Previous studies

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Abbreviations: ATS, ammonium thiosulfate; CP, chloropicrin; 1,3-D, 1,3-dichloropropene; GC, gas chromatography; Na-DEDTC, sodium diethyldithiocarbamate.

have indicated that the incorporation of organic amendments into soil may enhance biological degradation (by promoting the growth or stimulating the activity of fumigant-degrading microorganisms) and chemical degradation (by increasing the concentration of nucleophiles in the soil) (Dungan et al., 2001, 2003; Gan et al., 1998b). Application of nucleophilic compounds such as ammonium thiosulfate (ATS) can accelerate fumigant transformation and reduce emissions when applied at the soil surface (Gan et al., 1998a, 2000b). Other research has indicated that additional nucleophilic agrochemicals can accelerate the transformation of halogenated fumigants in aqueous solution and soil (Zheng et al., 2003). Previous research has focused on characterizing abiotic and biotic transformation of a single compound in soils. Little information exists regarding the effect of fumigant mixtures on the rate of degradation, although application of fumigant mixtures is common.

The primary objectives of this study were to (i) measure the rate of degradation of 1,3-D and CP when applied to soil separately and in a mixture to investigate the potential for competitive abiotic and biological degradation in fresh soils, and (ii) determine the transformation rate of 1,3-D, CP, and their mixture in soils amended with the nucleophilic compounds ATS and Na-DEDTC, to further evaluate competitive degradation between 1,3-D and CP in mixture.

MATERIALS AND METHODS

Chemicals and Soils

Analytical standards of chloropicrin (trichloronitromethane, CP, 99% purity) and 1,3-dichloropropene (1,3-D, 49% *cis* isomer and 49% *trans* isomer) were purchased from Chem Service (West Chester, PA). Ammonium thiosulfate (purity of >99%) was obtained from Fluka (Buchs, Switzerland) and sodium diethyldithiocarbamate (99% purity) was purchased from Aldrich Chemical Co. (Milwaukee, WI).

The soil used in the incubation study was an Arlington sandy loam (coarse-loamy, mixed, thermic Haplic Durixeralf), which was collected from the University of California, Riverside Agricultural Experiment Station. Fresh soils were obtained from the top 15 cm (A horizon) of a field that had not previously received fumigant application. Soil was passed through a 2-mm sieve without air-drying and stored at low temperature (4°C) until used. The soil had a pH of 7.2 and consisted of 0.92% organic matter, 64% sand, and 7% clay.

Competitive Degradation Experiments

The degradation of 1,3-D, CP, and their mixture was first studied in fresh Arlington sandy loam. Before fumigant treatment, soil moisture content was adjusted to 7.5% by weight, corresponding to a matrix potential of 2.6 MPa. Ten grams (dry weight) of soil were then weighed into 21-mL vials. Each vial was spiked with 0.5 mL of 1,3-D and CP aqueous solution. Initial concentrations of fumigant in samples spiked with 1,3-D only were 0.2 mmol/kg *cis*- and 0.2 mmol/kg *trans*-1,3-D. Initial CP concentrations in soil samples spiked with CP only were 0.1 mmol/kg. For the mixtures, initial concentrations were 0.1 mmol/kg CP + 0.4 mmol/kg 1,3-D, which corresponds to the ratio in the commercial product Telone C-17. After spiking, the vials were immediately capped with aluminum seals and Teflon-faced butyl rubber septa and incubated at 30 ± 0.5°C in the dark. Triplicate samples were removed at different time intervals and immediately transferred to a freezer (−21°C) until extraction. To extract fumigant residues from soil, the sample vials were decapped while the soil was still frozen, anhydrous sodium sulfate (10 g) and ethyl acetate (10 mL) were added, and the vials were immediately recapped. The capped vials were placed on a shaker and vigorously shaken for 1 h, then vortexed for 2 min at room temperature to attain complete recovery. Supernatant (1.5 mL) from each vial was transferred to a gas chromatography (GC) vial to analyze fumigant compounds in the extract by gas chromatography. Preliminary experiments showed that this extraction method gave >95% recovery for 1,3-D and CP. Disappearance of fumigants in soils was fitted to a first-order kinetic model. The degradation rate constants were compared using a *t* test at a significance of $\alpha = 0.05$ to test for differences in degradation rates in samples spiked with fumigants separately and in mixture.

Parallel experiments were conducted in sterile soil to determine the influence of abiotic degradation in fumigant mixtures and thereby deduce the effect of biodegradation. Soil with 7.5% moisture content was weighed into headspace vials (10.0 g dry wt.), and then autoclaved twice at 121°C, each for 60 min with a 24-h interval. Soil samples were aseptically spiked with fumigants and initial concentrations of CP and 1,3-D were 0.1 and 0.4 mmol/kg, respectively. Competitive degradation was also performed in the sterilized soil. The mixture solution of CP and 1,3-D was spiked at the same rates as above, which produced soil concentrations of 0.1 mmol/kg CP and 0.4 mmol/kg 1,3-D. The same procedures as given above were performed for incubation, sampling, and analysis of residual fumigant concentration.

The potential for competitive degradation between 1,3-D and CP was further determined in soils amended with ATS and Na-DEDTC. To prepare the amended soil, ATS or Na-DEDTC aqueous solutions (10 m*M*) were added to soil and thoroughly mixed in a plastic bag. Soil concentrations were 0.5 mmol/kg for ATS and 0.5 mmol/kg for Na-DEDTC. The same processes as described above were used to study degradation and competitive degradation of CP and 1,3-D in sterile and nonsterile amended soils.

Analytical Procedures

The concentrations of 1,3-D and CP in the extracts were determined by gas chromatography (GC) with an HP 5890 GC (Hewlett-Packard, Palo Alto, CA) equipped with a microelectron capture detector (μECD). The GC column was a 30-m × 0.25-mm × 1.4-μm DB-VRX capillary column (J&W Scientific, Folsom, CA). The GC conditions were 230°C inlet temperature, 280°C detector temperature, and 1.3 mL/min carrier gas flow rate (He). The initial oven temperature was 50°C and the temperature was increased to 80°C at 2.5°C/min, then increased to 110°C at 30°C/min and held for 4 min. Under these conditions, the retention times for *cis*-1,3-D, *trans*-1,3-D, CP, and dichloronitromethane were 11.3, 12.5, 13.4, and 11.6 min, respectively.

An HP 5890 GC in tandem with an HP 5971 mass selective detector was used to obtain mass spectra of CP transformation products. The GC column was a 30-m × 0.25-mm × 1.4-μm RTX-624 capillary column (Restek Co., Bellefonte, PA). The GC conditions were 0.9 mL/min He flow rate, 80°C initial oven temperature (4 min) ramping at 2°C/min to 110°C, 70 eV in EI mode, and 30 to 150 *m*/*z* scanning range.

RESULTS AND DISCUSSION

Competitive Degradation between 1,3-Dichloropropene and Chloropicrin in Soils

In the first set of experiments, the effect of 1,3-D on the rate of CP degradation in Arlington sandy loam was determined. The degradation curves of CP (Fig. 1) were well described by first-order kinetics ($r \geq 0.97$, Table 1). The degradation of fumigant CP (0.1 mmol/kg) was accelerated in the presence of 1,3-D (0.4 mmol/kg) in soils during the first day following treatment and then showed dissipation similar to CP (0.1 mmol/kg) spiked alone (Fig. 1). In both cases, the CP was almost completely dissipated within 3 d in these fresh soil samples. These results indicated that the presence of 1,3-D in soils did not considerably inhibit the microorganisms capable of degrading CP at these concentration levels. On the contrary, 1,3-D may have stimulated the soil microbial activity and accelerated the degradation of CP shortly after application.

In studies of the influence of different herbicides and fumigants on microbial activities in soil, Tu (1994) observed that treatment with 1,3-D and related C_3 hydrocarbons had a significant stimulatory effect on the microbial activities of soil. Several bacterial strains capable of degrading 1,3-D were isolated and identified from soils, including certain *Pseudomonas* spp. that could use 1,3-D as their sole carbon and energy source (Lebbink et al., 1989). Similarly, four species of soil *Pseudomonas* were also found to have the ability to rapidly degrade CP (Castro et al., 1983), which indicated that CP and 1,3-D could be degraded or cometabolized by analogous microorganisms. These published reports support the possibility that the enhancement in the rate of CP degradation at early times we observed (Fig. 1) may be due to a stimulatory effect of 1,3-D on soil microbial activities. The CP degradation rate constants (k) in the presence and absence of 1,3-D (Table 1) were statistically compared using a t test, and the result suggested that the difference was considered significant at the 0.05 probability level.

Table 1. First-order rate constant (k) and half-life ($t_{1/2}$) of chloropicrin (CP) degradation in Arlington sandy loam with and without 1,3-dichloropropene (1,3-D).

CP	1,3-D	Rate constant, $k \times 10^2$	Half-life, $t_{1/2}$	r
mmol/kg		h^{-1}	h	
0.1	0	7.50 ± 0.41	9.2	0.99
0.1	0.4	8.91 ± 1.08†	7.8	0.97
0.1 (Sterile soil)	0	1.21 ± 0.02	57.3	1.00
0.1 (Sterile soil)	0.4	1.09 ± 0.11†	63.6	0.99

† Difference of CP degradation rate constants in the presence and absence of 1,3-D was significant at $\alpha = 0.05$.

Degradation of 1,3-D isomers in Arlington sandy loam was determined in the presence or absence of CP (Fig. 2). The degradation of both isomers followed first-order kinetics with a correlation coefficient (r) of ≥0.94 (Table 2). No significant difference in the k of *cis*-1,3-D in soil was observed with and without CP. However, the k of *trans*-1,3-D decreased by approximately 14% when CP was applied with 1,3-D to fresh soils. Due to very rapid degradation of CP at this concentration (Fig. 1, Table 1), these results suggest that the accumulation of CP degradation products might have influenced

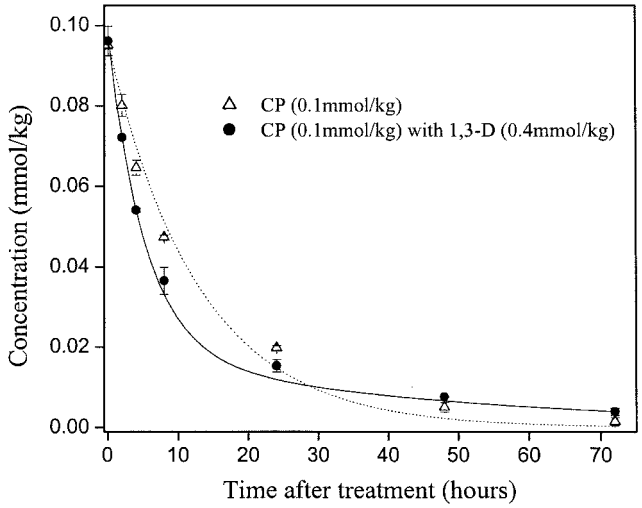

Fig. 1. Influence of 1,3-dichloropropene (1,3-D) (0.4 mmol/kg) on the degradation of chloropicrin (CP) in nonsterile Arlington sandy loam at 30 ± 0.5°C. The points are the means of three measurements (±standard errors).

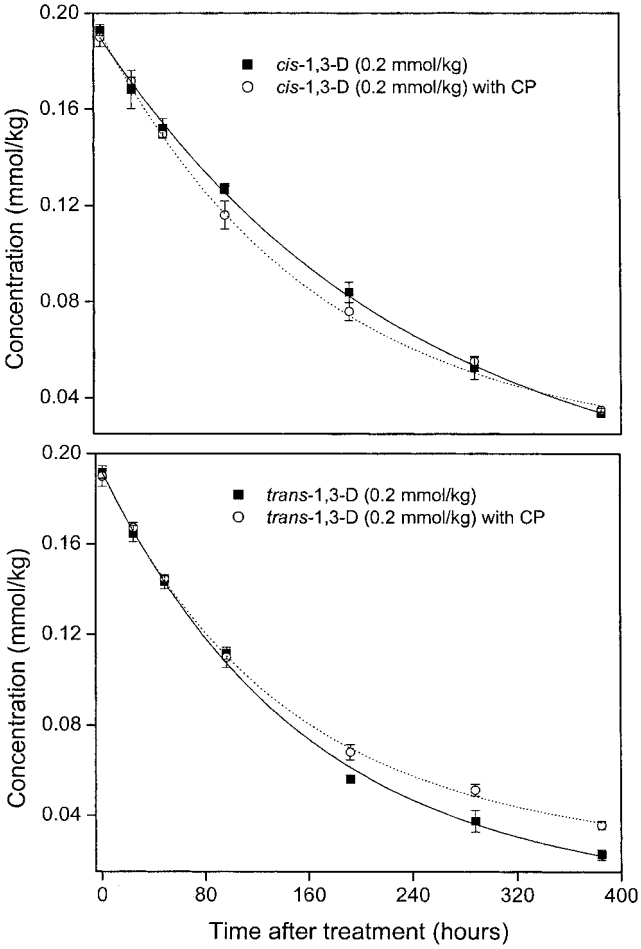

Fig. 2. Influence of chloropicrin (CP) on the degradation of 1, 3-dichloropropene (1,3-D) in nonsterile Arlington sandy loam at 30 ± 0.5°C. Initial CP concentration applied was 0.1 mmol/kg. The points are the means of three measurements (±standard errors).

Table 2. Influence of chloropicrin (CP) on the degradation of 1,3-dichloropropene (1,3-D) (50% *cis*-1,3-D and 50% *trans*-1,3-D) in Arlington sandy loam. Values in parentheses are the correlation coefficient, *r*.

		cis-1,3-D		*trans*-1,3-D	
1,3-D	CP	Rate constant, $k \times 10^2$	Half-life, $t_{1/2}$	Rate constant, $k \times 10^2$	Half-life, $t_{1/2}$
mmol/kg		h^{-1}	h	h^{-1}	h
0.4	0	0.45 ± 0.02 (0.99)	154	0.56 ± 0.02 (0.99)	124
0.4	0.1	0.47 ± 0.03 (0.99)	147	0.48 ± 0.02 (0.99)†	144
0.4 (Sterile soil)	0	0.41 ± 0.02 (0.99)	169	0.32 ± 0.01 (0.99)	217
0.4 (Sterile soil)	0.1	0.39 ± 0.05 (0.94)	177	0.31 ± 0.03 (0.96)	224

† Difference of *trans*-1,3-D degradation rate constants in the presence and absence of CP was significant at $\alpha = 0.05$.

trans-1,3-D degradation. Castro et al. (1983) reported the major path of metabolism for CP as sequential dechlorination to dichloronitromethane, chloronitromethane, and nitromethane. The disappearance of CP was accompanied by an increase in concentration in dichloronitromethane, which then fell off slowly with increasing incubation time.

The degradation rates of CP, 1,3-D, and their mixture were also measured in sterile soils (Table 1 and 2). Generally, both microbial and chemical degradation may be involved in fumigant degradation in fresh soil. However, fumigant degradation in sterile soil is usually only attributable to abiotic degradation mechanisms. The large decrease in *k* for fumigants in sterile soils compared with fresh soils implied an important role of soil microorganisms in fumigant degradation. For example, the half-life of CP (0.1 mmol/kg) was 9.2 h in nonsterile soils and increased 6.2 times to 57.3 h in autoclaved Arlington sandy loam (Table 1), which indicated that CP was degraded predominantly by biodegradation in this soil. Previous laboratory experiments have also shown a significant decrease in the rate of CP degradation with soil sterilization, which suggested that biodegradation accounted for 68 to 92% of the overall CP degradation (Gan et al., 2000a). Similar results were observed in this experiment, where biological degradation apparently accounted for 84% of the total CP degradation in fresh soil samples. A similar effect was observed in sterile soil treated with a mixture of CP and 1,3-D (Table 1), for which biological degradation accounted for 88% of the total degradation.

However, abiotic transformation such as hydrolysis and alkylation may still play an important role under certain experimental conditions. Because soil organic matter contains a variety of nucleophilic groups such as $-NH_2$, -NH-, -SH, and -OH, nucleophilic reaction between soil components and CP or 1,3-D is likely to occur. In sterile soil, CP degradation was slightly suppressed in the presence of 1,3-D compared with the application of CP only. In sterile soil, the degradation rate of CP (0.1 mmol/kg) was reduced about 10% in the presence of 0.4 mmol/kg (initial concentration) of 1,3-D (Table 1). These results suggest that CP and 1,3-D may compete for a limited number of reaction sites on the surface of soil particles.

Similar to the results for CP, degradation rates of 1,3-D isomers in sterile soils were slower than those in nonsterile soils (Table 2), which indicated that biodegradation was an important mechanism in the degradation of 1,3-D isomers in fresh soil. In these experiments, the decrease in degradation rate with autoclaving was greater for *trans*-1,3-D than for *cis*-1,3-D. The autoclaving resulted in a >40% decrease in *k* for *trans*-1,3-D at an initial concentration of 0.2 mmol/kg because of the elimination of biodegradation; however, autoclaving reduced the *k* for *cis*-1,3-D by only 9%. Previous research implied that *trans*-1,3-D is more susceptible to biological degradation than *cis*-1,3-D. Biological degradation may be more important for *trans*-1,3-D because of increased biodegradability of the transformation products (Van Dijk, 1974; Leistra et al., 1991; Ou et al., 1995; Ou, 1998). In addition, Chung et al. (1999) found that *trans*-1,3-D was degraded much more rapidly than the *cis* form in some loamy soils with histories of previous field application of 1,3-D because of increased microbial degradation. In these experiments, in sterile soil, *cis*-1,3-D was degraded more rapidly than *trans*-1,3-D (Table 2), indicating that *cis*-1,3-D may be more susceptible to abiotic degradation than *trans*-1,3-D. No effect on the rate of 1,3-D degradation applied in combination with CP was observed in the sterile soil (Table 2). It is commonly known that autoclaving may alter the chemical and physical characteristics of soil (Skipper and Westerman, 1973) and cause organic matter release. Ou et al. (1997) reported that autoclaving might accelerate the chemical degradation of the fumigant methyl bromide because more chemical reaction sites are possibly being formed on the sterilized-soil surface.

Competitive Degradation between 1,3-Dichloropropene and Chloropicrin in Amended Soils

The degradation of 1,3-D, CP, and their mixture was further studied in amended Arlington sandy loam. In ATS- and Na-DEDTC-amended soils, CP disappeared much more rapidly than in unamended soil (Fig. 3). The use of ATS and Na-DEDTC as nitrification inhibitors has been proposed (Prasad and Power, 1995; Saad et al., 1996) to limit the rate at which NH_4^+ becomes available to nitrifiers. Application of ATS can accelerate degradation of halogenated hydrocarbons such as fumigants and some herbicides in soil (Wang et al., 2000; Gan et al., 2002). Preliminary experiments indicated that Na-DEDTC is a strong nucleophilic reagent, and Na-DEDTC reacted rapidly with methyl iodide in aqueous solution (Zheng et al., 2003). The reaction mechanism between Na-DEDTC and CP in solution is hypothesized to be a nucleophilic substitution process with the sulfur atom of diethyldithiocarbamate attacking the

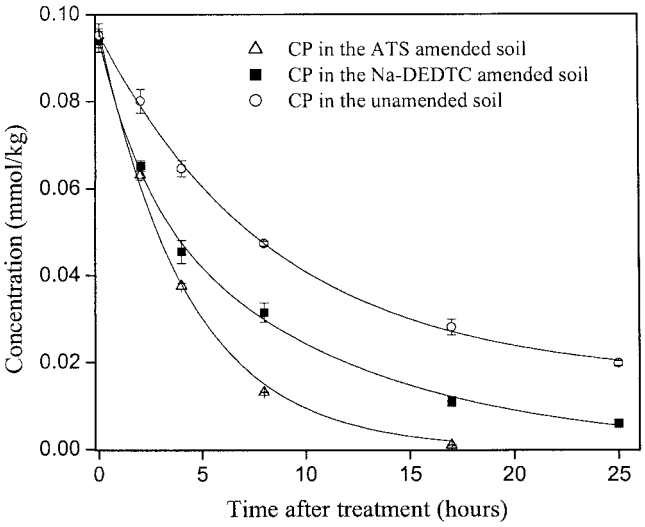

Fig. 3. Degradation of chloropicrin (CP) in unamended and amended Arlington sandy loam (amendments added at 0.5 mmol/kg). The points are the means of three measurements (±standard errors).

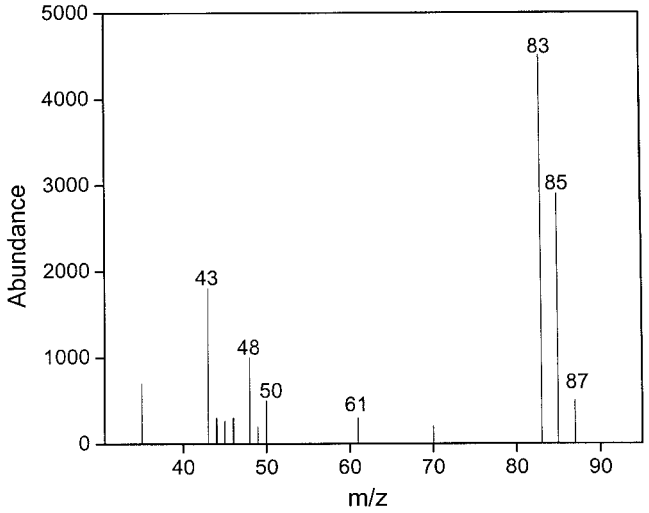

Fig. 4. Mass spectrum of metabolite (dichloronitromethane) from degradation of chloropicrin (CP) in amended soil [83 (M^+–NO_2), 48 (M^+–NO_2–Cl)].

carbon atom of CP, liberating one Cl^-. Further transformation may involve the addition of hydrogen due to H_2O attacking the S–C bond, producing dichloronitromethane ($HCCl_2NO_2$) (Eq. [1]). The transformation products of CP in Na-DEDTC-amended soils were extracted and analyzed using GC–mass spectrometry (MS). Dichloronitromethane (Fig. 4) was identified and confirmed as the major product:

$$(C_2H_5)_2NCSS^- + CCl_3NO_2 \rightarrow (C_2H_5)_2NCSS\text{-}CCl_2NO_2 + Cl^- \xrightarrow{H_2O} HCCl_2NO_2 \quad [1]$$

The thiosulfate anion ($S_2O_3^{2-}$) contains different nucleophilic centers and the nucleophilic strength should be the greatest on the sulfur atom. It is well known that the thiosulfate anion can easily convert alkyl halides to their Bunte salt ($RSSO_3^-$) (Distler, 1967) and thiosulfate compounds are often utilized as classic reduction reagents. The reaction mechanism between CP and ATS is postulated to involve an initial conversion to the Bunte salt by reaction with thiosulfate ion in the soil solution, followed by hydrolysis to dichloronitromethane (Eq. [2]). Production of dichloronitromethane in ATS-amended soil was verified by GC–MS analysis:

$$CCl_3NO_2 + S_2O_3^{2-} \rightarrow Cl_2NO_2C\text{-}S\text{-}SO_3^- + Cl^- \xrightarrow{H_2O} HCCl_2NO_2 \quad [2]$$

Under the experimental conditions used in these studies, 98% of the CP was degraded in the ATS-amended soil and 90% was degraded in Na-DEDTC-amended soil in 17 h, but only about 72% of the CP was degraded in fresh soil (Fig. 3). The degradation of CP in ATS-amended soil was faster than that in Na-DEDTC-amended soil, though Na-DEDTC has much more nucleophilic substitution reaction activity with halogenated hydrocarbons in aqueous solution than ATS does. The difference in reactivity in soil may result from the different distribution of ATS and Na-DEDTC in soil. Generally, fumigants in soil are distributed between three phases: soil solution, sorbed to soil surface, and vapor phase. Wang et al. (2000) suggested that the reaction between ATS and fumigants may occur only in the aqueous phase. Ammonium thiosulfate is an inorganic chemical and its reactive group (thiosulfate anion, $S_2O_3^{2-}$) may exist in the aqueous phase of soil as the ion, while Na-DEDTC is an organic chemical that may have a higher sorption capacity in soil. Therefore, the molar concentration of Na-DEDTC in the soil solution phase should be lower than that of ATS at the same molar application rate. Correspondingly, the degradation rate of CP would be decreased in Na-DEDTC-amended soil relative to ATS-amended soil. Under the conditions used in these experiments, the first-order half-life ($t_{1/2}$) of CP was 9.2 h in the unamended soil, 3.3 h in the ATS-amended soil, and 4.8 h in the Na-DEDTC-amended soil.

Similar results were also observed for the degradation of 1,3-D isomers in amended soils. The decline of *cis*- and *trans*-1,3-D was well described by first-order kinetics (Table 3). The degradation rate of 1,3-D isomers was faster in the ATS- and Na-DEDTC-amended soil compared with the fresh soil, and both isomers were degraded more rapidly in soil amended with ATS than with Na-DEDTC, similar to CP degradation in amended soils. Although no significant difference in the *k* for the two isomers was observed in the Na-DEDTC-amended soil (Table 3), *cis*-1,3-D was degraded significantly faster than *trans*-1,3-D in the ATS-amended soil. These results are in agreement with Gan et al. (2000b) and Wang et al. (2000) who also reported that transformation by ATS was more rapid for *cis*-1,3-D than for *trans*-1,3-D. The initial step in the proposed mechanism of 1,3-D transformation in the presence of thiosulfate is characteristic of S_N2 type reactions, and the observation that the *trans* isomer was less reactive to thiosulfate than the *cis* isomer

Table 3. First-order rate constant (k) and half-life ($t_{1/2}$) of 1,3-dichloropropene (1,3-D) (0.2 mmol/kg *cis*-1,3-D, 0.2 mmol/kg *trans*-1, 3-D) degradation in Arlington sandy loam amended with ammonium thiosulfate (ATS) or sodium diethyldithiocarbamate (Na-DEDTC) (0.5 mmol/kg). Values in parentheses are the correlation coefficient, r.

Treatment	*cis*-1,3-D		*trans*-1,3-D	
	Rate constant, $k \times 10^2$	Half-life, $t_{1/2}$	Rate constant, $k \times 10^2$	Half-life, $t_{1/2}$
	h^{-1}	h	h^{-1}	h
ATS-amended soil	1.88 ± 0.17 (0.96)	36.9	1.04 ± 0.06 (0.98)	66.6
ATS-amended sterile soil	1.87 ± 0.25 (0.96)	37.1	1.03 ± 0.07 (0.98)	67.3
Na-DEDTC-amended soil	0.86 ± 0.05 (0.97)	80.6	0.84 ± 0.05 (0.97)	82.5
Na-DEDTC-amended sterile soil	0.69 ± 0.06 (0.94)	100.5	0.73 ± 0.12 (0.98)	95.0

may be attributable to the stability of the transition state. It is likely that the transition state that was formed by *cis*-1,3-D and $S_2O_3^{2-}$ underwent further degradation more easily than that formed by the *trans* isomer because of the higher energy and steric hindrance of the transition state. These results for ATS-amended soil further supported the conclusion that *cis*-1,3-D was more susceptible to abiotic degradation than *trans*-1,3-D.

Comparing the rate of 1,3-D transformation in sterile and nonsterile amended soil indicated that the degradation of 1,3-D was dominated by abiotic reactions in ATS- and Na-DEDTC-amended soil (Table 3). Abiotic transformation accounted for ≥80% of the total 1,3-D degradation in amended soils. However, the contribution of microbial degradation should not be neglected in amended soil, especially for CP. For instance, the first-order degradation rate k of CP was 0.21 and 0.14 h^{-1} in the ATS- and Na-DEDTC-amended fresh soil, but in the corresponding sterile soil, the values decreased to 0.13 and 0.061 h^{-1}, respectively (Fig. 5). The contribution of biological degradation of CP was approximately 40% in ATS-amended soil and approximately 55% in Na-DEDTC-amended soil. Thus, it appears that the application of ATS and Na-DEDTC did not completely inhibit the microbial population responsible for CP degradation, and both abiotic and microbial degradation contributed to CP removal in ATS- and Na-DEDTC-amended soils.

Competitive degradation was observed for CP degradation in amended soil spiked with a mixture of CP and 1,3-D (Fig. 5). The degradation rate of CP was decreased when applied together with 1,3-D in nonsterile and sterile soils amended with ATS and Na-DEDTC. Because abiotic degradation was responsible for approximately 50% of the total degradation in amended soil, these results suggest that CP competed with 1,3-D in reaction

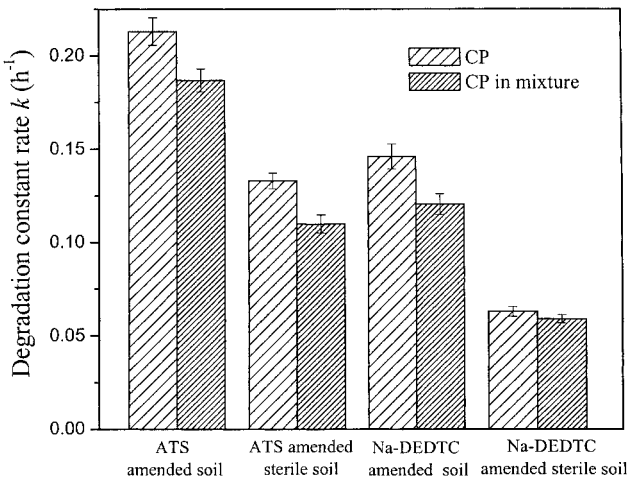

Fig. 5. Effect of 1,3-dichloropropene (1,3-D) (0.4 mmol/kg) on the degradation constant rate k (h^{-1}) of chloropicrin (CP) (0.1 mmol/kg) in amended Arlington sandy loam (amendments added at 0.5 mmol/kg). Vertical bars are the standard error of k.

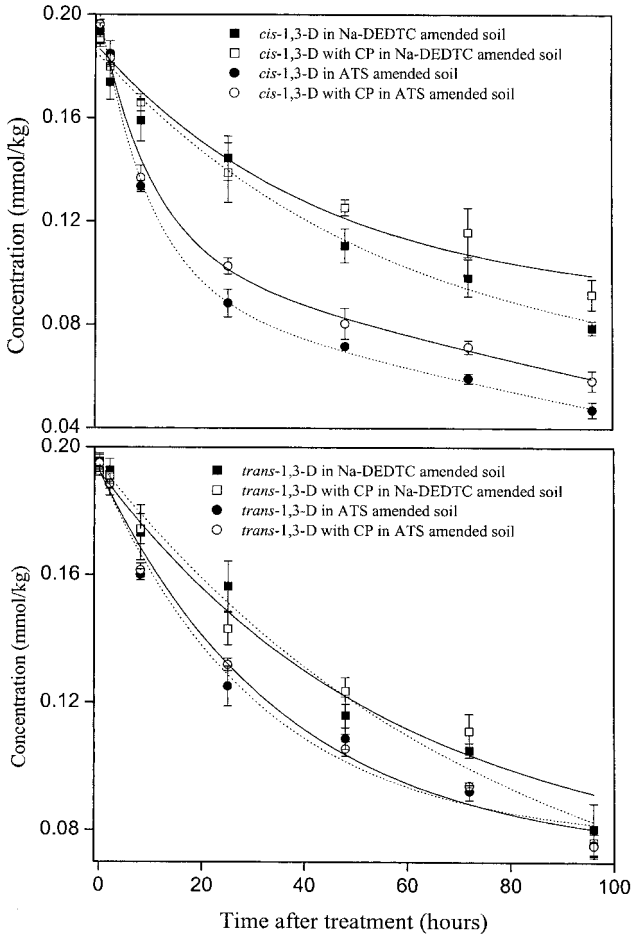

Fig. 6. Competitive degradation of 1,3-dichloropropene (1,3-D) isomers in amended Arlington sandy loam (amendments added at 0.5 mmol/kg). Initial chloropicrin (CP) and 1,3-D applied concentrations were 0.1 and 0.4 mmol/kg, respectively. The points are the means of three measurements (±standard errors).

with ATS or Na-DEDTC, resulting in a slower degradation rate.

Competitive degradation of 1,3-D isomers in the amended soils was also measured in the presence of CP. The *cis* and *trans* isomers responded differently in these systems. Degradation of *cis*-1,3-D in nonsterile amended soil samples spiked with a mixture of 1,3-D and CP was apparently repressed compared with its degradation in samples spiked with 1,3-D only (Fig. 6). The degradation rate of *cis*-1,3-D in fresh amended soils was decreased by approximately 20% in samples spiked with the mixture of 1,3-D and CP (Fig. 6 and 7). No significant competitive effect was observed for *trans*-1,3-D (Fig. 7). Thus, it may be concluded that the *cis* isomer competed with CP more strongly than the *trans* isomer in reaction with ATS and Na-DEDTC in soil solution. Because abiotic reaction with ATS and Na-DEDTC favors the *cis* isomer (Table 3), a stronger competitive effect was observed for the *cis* isomer in amended soil treated with a mixture of CP and 1,3-D. Reaction sites in amended soil include nucleophilic groups of the soil organic matter and ATS or Na-DEDTC added to soil.

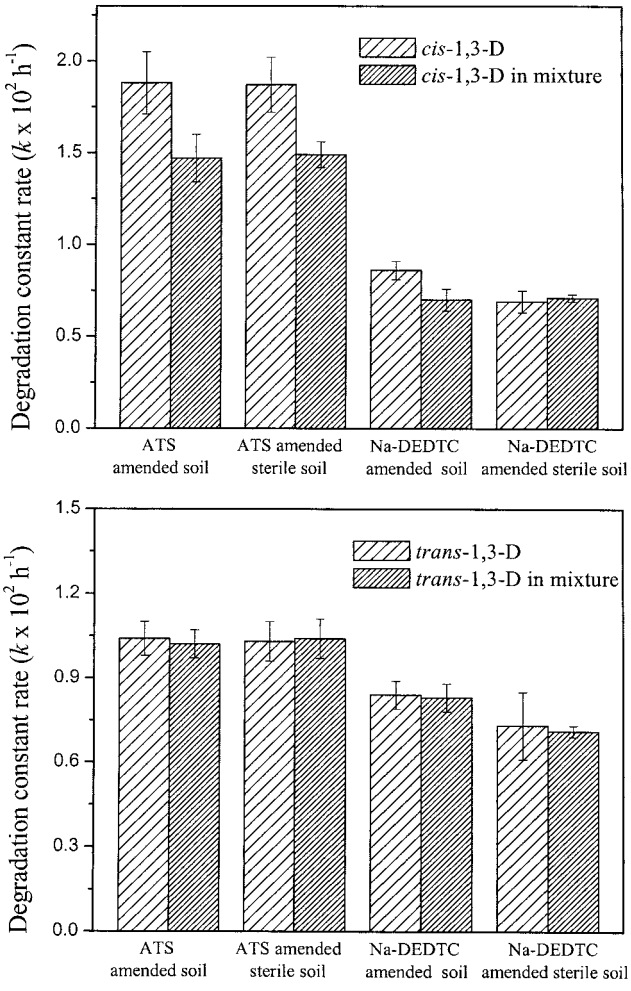

Fig. 7. Influence of chloropicrin (CP) (0.1 mmol/kg) on the degradation constant rate ($k \times 10^2$ h^{-1}) of 1,3-dichloropropene (1,3-D) (0.2 mmol/kg *cis*-1,3-D, 0.2 mmol/kg *trans*-1,3-D) in amended Arlington sandy loam (amendments added at 0.5 mmol/kg). Vertical bars are the standard error of k.

CONCLUSIONS

The fumigants CP, 1,3-D, and their mixture were degraded via microbial and abiotic mechanisms in fresh soils. A comparison of the rate of degradation in nonsterile and sterile soils indicated that biodegradation played an important role in fumigant degradation. Soil amendment with ATS and Na-DEDTC accelerated the degradation of CP and 1,3-D through efficient dehalogenation reactions, and the ATS-amended soils showed greater nucleophilic substitution activity in soils than the Na-DEDTC-amended soils. In sterile soils and ATS- or Na-DEDTC-amended soils, the rate of CP degradation was repressed in soil samples spiked with a mixture of CP and 1,3-D, presumably because of a competition with 1,3-D for available reaction sites. While the degradation of *trans*-1,3-D was retarded in the fresh soil in the presence of CP, no competitive effect was observed in ATS- or Na-DEDTC-amended soil. For the *cis* isomer, no competitive effect was observed in fresh soil, but competition with CP inhibited degradation in the amended soils. These results suggest that *trans*-1,3-D is more susceptible to microbial degradation, whereas *cis*-1,3-D may react more quickly in abiotic transformations. Overall, the application of a mixture of CP and 1,3-D had little influence on the degradation rate of either of the individual fumigants at the concentrations studied in fresh soil. Therefore, in applications of mixtures of 1,3-D and CP, the fumigant compounds appear to behave relatively independently in terms of their degradation, indicating that the strategy of application of fumigant mixtures may have little effect on the environmental fate and efficacy of these compounds.

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