

GENERAL PAPERS**Organized by****T. Mill**

Symposia Papers Presented Before the Division of Environmental Chemistry
American Chemical Society
Boston, MA August 18-22, 2002

**COMPETITIVE DEGRADATION BETWEEN FUMIGANTS
CHLOROPICRIN AND 1,3-DICHLOROPROPENE IN SOILS**

Wei Zheng, Sharon K. Papiernik, Mingxin Guo and Scott R. Yates
USDA-ARS; Soil Physics and Pesticide Research Unit,
George E. Brown Jr. Salinity Laboratory; Riverside, CA 92507
wzheng@usssl.ars.usda.gov

Introduction

The current scientific opinion that methyl bromide contributes significantly to the depletion of stratospheric ozone has led to much research on developing better management practices and identifying chemical alternatives to methyl bromide. 1,3-Dichloropropene (1,3-D) formulated with chloropicrin (CP) has been considered a practical alternative fumigant. For instance, mixtures of 1,3-D with 17% CP (Telone C-17) or 35% CP (Telone C-35) have been developed as commercial formulations. Excessive emissions of fumigant vapor into the atmosphere may contribute to air pollution and cause negative effects to human health and the environment. To minimize the negative impact of these fumigants on the environment, it is necessary to develop management strategies to reduce fumigant emissions to the atmosphere.

Ideally, the fumigant will be completely destroyed by degradation in the soil once adequate pest control is achieved. However, the rate of fumigant degradation is relatively slow in comparison to its rapid vapor diffusion. Thus, it may be important to manipulate and modify fumigant degradation to reduce its harmful effects of emissions and leaching. Generally, soil chemical and biological conditions influence the rate of fumigant degradation in soil. Previous studies indicate that application of ammonium thiosulfate (ATS) can accelerate fumigant transformation at the surface soil and reduce fumigant emissions^{1,2}. Previous research has focused on characterizing abiotic and biotic transformation of a single fumigant compound in soil. Little information exists regarding the effect of fumigant mixtures on the degradation rate, although application of fumigant mixtures is common. In this study, we determined the rate of degradation of

1,3-D and CP separately and as mixtures and evaluated possible competitive abiotic and biotic degradation in fresh soils. The competitive degradation between 1,3-D and CP in soils amended with ATS and sodium dithiocarbamate (SDTC) was also investigated.

Methods

The degradation of 1,3-D, CP, and their mixture was studied in Arlington sandy loam collected from the University of California, Riverside Agricultural Experiment Station. The soil had a pH of 7.2 and consisted of 0.92% organic matter, 64% sand, and 7% clay. Degradation was further determined in soils amended with ATS and SDTC. Ten grams (dry weight, water content 7.5%) of fresh soil or autoclaved soils was weighed into 21 mL vials. Solutions of 1,3-D, CP, and their mixture were spiked to the soil samples. The initial fumigant concentrations in the mixture were 0.1 mmol/kg CP and 0.4 mmol/kg 1,3-D which corresponds to Telone C-17, and 0.2 mmol/kg CP and 0.3 mmol/kg 1,3-D which corresponds to Telone C-35. The initial concentration of ATS and SDTC in amended soils was 0.5mmol/kg. Vials were capped immediately with aluminum seals and Teflon-faced butyl rubber septa and then incubated at 30 ± 0.5 °C in the dark. Triplicate samples were removed at different time intervals, extracted, and the extract analyzed by gas chromatography - ECD.

Results

The first set of experiments investigated that effect of 1,3-D on the rate of CP degradation in Arlington sandy loam. The degradation curves of CP are shown in Figure 1. The degradation of CP can be accelerated in the presence of 1,3-D in soils in the first day after treatment. Overall, the first-order rate constant (k) of CP was not influenced considerably when it was applied with 1,3-D.

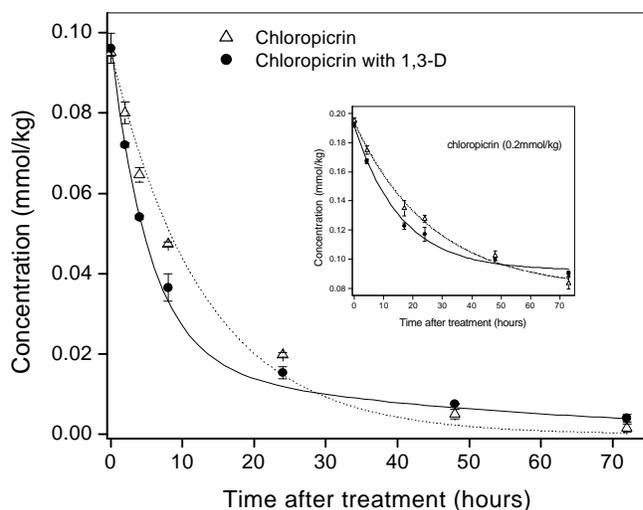


Figure 1. Influence of 1,3-D on the degradation of CP in Arlington sandy loam. Initial CP and 1,3-D concentration were 0.1 and 0.4mg/kg, 0.2 and 0.3mmol/kg (embodied figure), respectively. The points are the means of three measurements (\pm standard errors).

Degradation of 1,3-D isomers in Arlington sandy loam was determined in the presence or absence of CP and the degradation of both isomers was fitted to first-order kinetics (Table 1). No significant difference in the k of *cis*-1,3-D was observed with and without CP. However, the k of *trans*-1,3-D was decreased when CP was applied. Due to very rapid degradation of CP at this concentration level, it suggested that its degradation products might influence *trans*-1,3-D degradation.

Subsequently, the degradation of CP, 1,3-D isomers, and their mixture in autoclaved soils was measured. The large decrease in k for CP in autoclaved soils compared to fresh soils implied that the contribution of biodegradation was more predominant than that of chemical degradation. Similarly, degradation rates of 1,3-D isomers in autoclaved soils were slower than those in fresh soils, indicating that both chemical and microbial mechanisms were involved in degradation of 1,3-D isomers in fresh soil. However, chemical transformation such as hydrolysis and alkylation played an important role under certain experimental conditions. The degradation of CP was slightly suppressed when added in mixture with 1,3-D compared with CP only in autoclaved soils (Table 2). These results suggest that CP and 1,3-D might compete for a limited number of reactive sites in the soils. Thus, the occurrence of competitive abiotic degradation may influence the degradation rate of CP and 1,3-D in soils. The degradation of 1,3-D, CP, and their mixture was further studied in amended Arlington sandy loam. The degradation rates were significantly accelerated in ATS and SDTC amended soils. Application of ATS and SDTC to field soils as nitrification inhibitors has been proposed^{3,4}, these compounds limit the nitrification rate (rate at which NH_4^+ becomes available to nitrifiers). Recently research has found that ATS can accelerate degradation of halogenated fumigants⁵. We have also found that SDTC is a stronger nucleophilic reagent. The mechanism of reaction between SDTC and CP is hypothesized to be a nucleophilic substitution process, with the sulfur atom of diethylthiocarbamate attacking the carbon atom of CP and one Cl^- leaving. Further transformation may involve the addition of hydrogen due to H_2O attacking the S-C bond. The degradation product was extracted and then identified by GC-MS as dichloronitromethane (HCCl_2NO_2).

In the amended soil, competitive degradation was observed to decrease the rate of CP degradation in soils spiked with a mixture of CP and 1,3-D (Table 2). The first-order half-life ($t_{1/2}$) of CP was increased in amended soils containing 1,3-D and CP. Because abiotic degradation is predominant in the amended soils, these results suggest that CP might compete with 1,3-D in reaction with ATS or SDTC and result in slower degradation rates.

Competitive degradation of 1,3-D isomers in the amended soils was also measured in the presence of CP (Table 1). The *cis* and *trans* isomers responded differently in these systems. The degradation of *cis*-1,3-D in the mixture was apparently repressed compared to the k in amended soils spiked with 1,3-D only. However, no significant competitive effect between *trans*-1,3-D and CP in the ATS and SDTC amended soils was observed. Thus, it may be concluded that it was *cis* isomer rather than *trans*

isomer of 1,3-D which competed with CP in ATS- and SDTC-amended soils. Abiotic transformation was more significant for *cis*-1,3-D, and the *cis* isomer may be more likely to undergo S_N2 nucleophilic substitution reaction than *trans*-1,3-D.

Table 1. Influence of CP (0.1mmol/kg) on the degradation constant $k \times 10^2$ (h⁻¹) of 1,3-D (0.2mmol/kg *cis*-1,3-D, 0.2mmol/kg *trans*-1,3-D) in the fresh and amended Arlington sandy loam. (values in parentheses are the correlation coefficient *r*).

Treatment	1,3-D		1,3-D in mixture	
	<i>cis</i> -1,3-D	<i>trans</i> -1,3-D	<i>cis</i> -1,3-D	<i>trans</i> -1,3-D
Fresh soil	0.44(0.997)	0.59(0.993)	0.47(0.994)	0.48(0.994)
ATS amended soil	1.88(0.957)	1.04(0.976)	1.47(0.952)	1.02(0.980)
SDTC amended soil	0.86(0.974)	0.84(0.975)	0.70(0.986)	0.83(0.976)

Table 2. First-order half-life values (in hours) of CP (0.1mmol/kg) in Arlington sand loam in the presence or absence of 1,3-D (0.4mmol/kg) (values in parentheses are the correlation coefficient *r*).

Treatment	CP	CP in Mixture
Fresh soil	9.2(0.995)	7.8(0.970)
Sterile soil	57.3(0.998)	63.6(0.990)
ATS amended soil	3.3(0.997)	3.7(0.998)
SDTC amended soil	4.8(0.989)	5.8(0.997)

Reference

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